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editorial

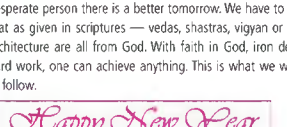
Ancient Wisdom in Modern Garb

It is known for a long time in the field of agriculture, that a good pedigree tree has a tendency to produce good fruits and also that any tree can give better fruits if only the proper fertilizers are given.

Studies are made in every research laboratory for the improvement of natural products such as cotton, silk, rice, wheat, mango and so on extensively. The technique of analysis is statistics. Correlation coefficients have to be calculated between yield and treatment. Different treatments are given and their correlation calculated for large scale application. The application of statistics is the key for the success of any research.

Recently a new science is growing popular — Dermatoglyphics (DMIT) to determine the genetic potential based on DMIT when children are very young because the fingerprint can be taken and studied for their ability to handle the chosen subjects better. This test is growing fast from Asia to USA and Australia, to cite only a few. However, this technique is not new. This is based on the principle that the different parts of the brain cause the whirls and curls of the fingerprint. Palmistry is a very old subject. If only one can consult an expert whose interest is only to help and not make money one can get many tips to succeed in life as well as avoid problems.

Just as the palm lines are characteristic of a person, his "kundalini" is also a characteristic. The planetary positions at the birth of a person gives his 'horoscope'. Experts in astrology use this to advice a person to get out of a problem or to improve his business by seeking the help of God. Even for a desperate person there is a better tomorrow. We have to remind ourselves that as given in scriptures — vedas, shastras, vigyan or sciences, silpa or architecture are all from God. With faith in God, iron determination and hard work, one can achieve anything. This is what we want our students to follow.



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Editor

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CHEMISTRY MUSING

Chemistry Musing was started from August '13 issue of Chemistry Today with the suggestion of Shri Mahabir Singh. The aim of Chemistry Musing is to augment the chances of bright students preparing for JEE (Main and Advanced) / AIPMT / AIIMS / Other PMTs & PETs with additional study material.

In every issue of Chemistry Today, 10 challenging problems are proposed in various topics of JEE (Main and Advanced) / AIPMT. The detailed solutions of these problems will be published in next issue of Chemistry Today.

The readers who have solved five or more problems may send their solutions. The names of those who send atleast five correct solutions will be published in the next issue.

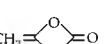
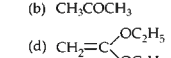
We hope that our readers will enrich their problem solving skills through "Chemistry Musing" and stand in better stead while facing the competitive exams.

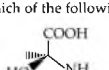
PROBLEM Set 6

JEE MAIN PMTs

1. A hydrogenation reaction is carried out at 580 K. If the same reaction is carried out in the presence of a catalyst at the same rate, the temperature required is 420 K. The activation energy of the reaction if the catalyst lowers the activation energy barrier by 20 kJ mol^{-1} is
   (a) 100 kJ mol^{-1} (b) 72.6 kJ mol^{-1}
   (c) 50 kJ mol^{-1} (d) 120 kJ mol^{-1}

2. Al_2O_3 is converted to AlN on heating with carbon in the atmosphere of N_2. How many grams of carbon is required to convert 23 g of Al_2O_3 to AlN?
   (a) 8 g (b) 12 g
   (c) 15 g (d) 102 g

3. $CH_3CO_2C_2H_5$ on reaction with sodium ethoxide in ethanol gives *P*, which on heating in the presence of acid gives *Q*. Compound *Q* is
   (a) CH_3COCH_2COOH
   (b) CH_3COCH_3 (c) 
   (d) 

4. Which of the following combinations are chiral?
   
   (I)

   (II)

   (III)

   (IV)
   (a) (I) and (IV) (b) (II) and (III)
   (c) (I) and (III) (d) (II) and (IV)

5. Which of the following statements is correct?
   (a) SF_4 is polar and non reactive.
   (b) SF_6 is nonpolar and very reactive.
   (c) SF_6 is a strong fluorinating agent.
   (d) SF_4 is prepared by fluorinating SCl_2 with NaF.

JEE ADVANCED

6. 1, 4-Pentadiene reacts with excess of HCl in the presence of benzoyl peroxide to give compound *X* which upon reaction with excess of Mg in dry

Solution Senders of Chemistry Musing

SET 5

1. Himanjyoti Bora, Nagaon (Assam)
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SET 4

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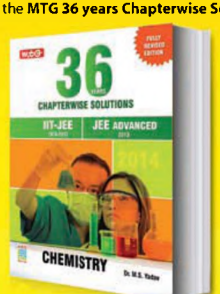

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ether forms *Y*. Compound *Y* on treatment with ethyl acetate followed by dilute acid yields *Z*. Identify the structures of compounds *X* and *Z* respectively.

(a) $(Cl)H_2CCH(Cl)CH_2CH=CH_2$, $(CH_3CO)H_2CCH(COCH_3)CH_2CH=CH_2$

(b) $(Cl)H_2CCH_2CH_2CH(Cl)CH_3$, $(CH_3CO)H_2CCH_2CH_2CH(COCH_3)CH_3$

(c) $ClH_2CCH(Cl)CH_2CH(Cl)CH_2(Cl)$, $(CH_3CO)H_2CCH=CHCH(COCH_3)CH_2Cl$

(d) $CH_3CH(Cl)CH_2CH(Cl)CH_3$, $CH_3CH(COCH_3)CH_2CH(COCH_3)CH_3$

COMPREHENSION

The electrochemical cell shown below is a concentration cell.

$M|M^{2+}$ (saturated solution of a sparingly soluble salt, MX_2) $||$ M^{2+} (0.001 mol dm^{-3}) $|M$

The emf of the cell depends on the difference in concentrations of M^{2+} ions at the two electrodes. The emf of the cell at 298 K is 0.059 V.

7. The value of ΔG for the given cell is
   (a) 9.6 kJ mol^{-1} (b) −21.5 kJ mol^{-1}
   (c) 11.4 kJ mol^{-1} (d) −11.4 kJ mol^{-1}

8. The solubility product (K_{sp}) in mol^3 dm^{-9} of MX_2 at 298 K based on the information available for the given concentration cell is
   (a) 1×10^{-15} (b) 4×10^{-15}
   (c) 1×10^{-12} (d) 4×10^{-12}

INTEGER VALUE

9. Among the following, the total number of molecules which possess sp^3d^2 hybridisation in their geometrical structures are
   SO_2, PCl_5, SF_6, $BeCl_2$, XeO_2F_4, $XeOF_2$, BrF_5, ClF_3, IF_5, NH_3

10. 1.44 g of pure FeC_2O_4 was dissolved in dil. HCl and solution diluted to 100 mL. Volume of 0.01 M $KMnO_4$ required to oxidise FeC_2O_4 solution completely (in 10^2 mL) is

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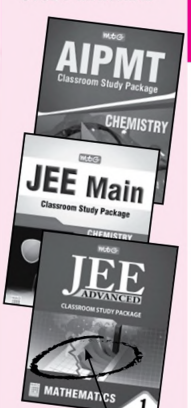

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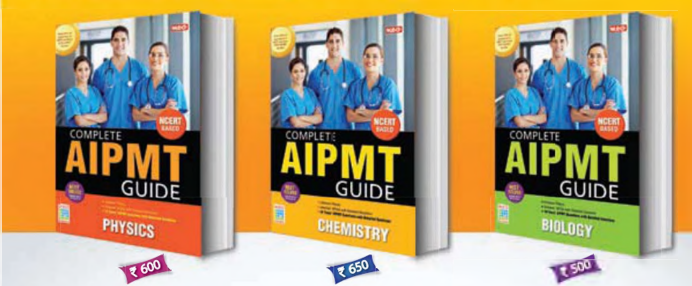

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1. At 25°C, the molar conductivity of 0.001 M hydrofluoric acid is 184.5 Ω^{-1} cm^2 mol^{-1}. If its Λ°_m is 502.4 Ω^{-1} cm^2 mol^{-1}, then equilibrium constant at the given concentration is
   (a) 3.607×10^{-1} M (b) 5.404×10^{-4} M
   (c) 2.127×10^{-4} M (d) 6.032×10^{-4} M

2. In which of the following pairs, both species have similar geometry?
   (a) CH_4, BF_3 (b) NH_3, BH_3
   (c) CO_2, H_2O (d) PCl_5, I_3^-

3. Products formed when anisole reacts with hydroiodic acid at 373 K are
   (a) iodobenzene and methanol
   (b) phenol and methyl iodide
   (c) aniline and methyl iodide
   (d) phenol and methanol.

4. Reaction of diborane with ammonia gives initially
   (a) borazine (b) borazole
   (c) $B_2H_6.3NH_3$ (d) $[BH_2(NH_3)_2]^+$ $[BH_4]^-$

5. Zinc on reacting with cold, dil. HNO_3, gives
   (a) $ZnNO_3$ (b) NH_4NO_3
   (c) NO_2 (d) NO

6. In acidic medium, $KMnO_4$ oxidises $FeSO_4$ solution. Which of the following statements is correct?
   (a) 10 mL of 1 N $KMnO_4$ solution oxidises 10 mL of 5 N $FeSO_4$ solution
   (b) 10 mL of 1 M $KMnO_4$ solution oxidises 10 mL of 5 M $FeSO_4$ solution
   (c) 10 mL of 1 M $KMnO_4$ solution oxidises 10 mL of 1 M $FeSO_4$ solution
   (d) 10 mL of 1 N $KMnO_4$ solution oxidises 10 mL of 0.1 M $FeSO_4$ solution

7. An element (with atomic mass = 300) crystallises in a simple cubic. If the density of the unit cell is 9.5 g cm^{-3}, what is the radius of the element?
   (a) 1.87×10^{-8} cm (b) 1.97×10^{-8} cm
   (c) 1.77×10^{-8} cm (d) 1.02×10^{-8} cm

8. NH_4^+ is isostructural with
   (a) CH_3^- (b) CH_3^+
   (c) H_3O^+ (d) SO_4^{2-}

9. The molecule which has zero dipole moment is
   (a) CH_2Cl_2 (b) BF_3
   (c) NF_3 (d) ClO_2

10. Nitrobenzene on reduction with $LiAlH_4$ in the presence of ether gives
    (a) aniline
    (b) benzene
    (c) azobenzene
    (d) *N*-phenylhydroxylamine.

11. Which molecule/ion out of the following does not contain unpaired electrons?
    (a) N_2^+ (b) O_2
    (c) O_2^{2-} (d) B_2

12. The type of isomerism not exhibited by alkenes is
    (a) chain isomerism (b) metamerism
    (c) position isomerism (d) stereoisomerism.

13. The following quantum numbers are possible for how many orbitals? $n = 3$, $l = 2$, $m = +2$
    (a) 1 (b) 2
    (c) 3 (d) 4

14. Energy of an electron in hydrogen atom is given by $E = \frac{13.6}{n^2}$ eV. Which one of the following statements is true if n is changed from 1 to 3? Energy will
    (a) decrease three times
    (b) increase three times
    (c) increase nine times
    (d) decrease nine times.

15. The equilibrium $Cr_2O_7^{2-} \rightleftharpoons 2CrO_4^{2-}$ is shifted to right in
    (a) an acidic medium (b) an alkaline medium
    (c) neutral medium (d) aqueous medium.

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16. Which of the following statements is not correct?
(a) Some antiseptics can be added to soaps.
(b) Dilute solutions of some disinfectants can be used as an antiseptic.
(c) Disinfectants are antimicrobial drugs.
(d) Antiseptic medicines can be ingested.

17. The rate constant of a first order reaction increases by 6% when its temperature is raised from 27° to 28°C. The activation energy of the reaction is
(a) 43.7 kJ/mol (b) 17.5 kJ/mol
(c) 47.5 kJ/mol (d) 27.5 kJ/mol

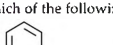
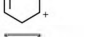
18. 0.5 mole of each of H_2, SO_2 and CH_4 are kept in a container. A hole was made in the container. After 3 hours, the order of partial pressures in the container will be
(a) $p_{SO_2} > p_{CH_4} > p_{H_2}$ (b) $p_{H_2} > p_{SO_2} > p_{CH_4}$
(c) $p_{CH_4} > p_{SO_2} > p_{H_2}$ (d) $p_{H_2} > p_{CH_4} > p_{SO_2}$

19. The pair in which both species have same magnetic moment (spin only value) is
(a) $[Cr(H_2O)_6]^{2+}$, $[CoCl_4]^{2-}$
(b) $[Cr(H_2O)_6]^{2+}$, $[Fe(H_2O)_6]^{2+}$
(c) $[Mn(H_2O)_6]^{2+}$, $[Cr(H_2O)_6]^{2+}$
(d) $[CoCl_4]^{2-}$, $[Fe(H_2O)_6]^{2+}$

20. A solution of sulphur dioxide in water reacts with H_2S precipitating sulphur. Here sulphur dioxide acts as
(a) an oxidising agent (b) a reducing agent
(c) an acid (d) a catalyst.

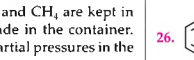
21. Which of the following is aromatic?
(a) (b)
(c) (d)

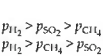
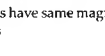
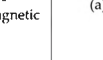
22. The compound which is not isomeric with diethyl ether is
(a) *n*-propyl methyl ether
(b) butan-l-ol
(c) 2-methylpropan-2-ol
(d) butan-2-one

23. Tautomerism is not exhibited by
(a) 
(b) 
(c) (d)

24. Arrange Ce^{3+}, La^{3+}, Pm^{3+} and Yb^{3+} in increasing order of their ionic radii.
(a) $Yb^{3+} < Pm^{3+} < Ce^{3+} < La^{3+}$
(b) $Ce^{3+} < Yb^{3+} < Pm^{3+} < La^{3+}$
(c) $Yb^{3+} < Pm^{3+} < La^{3+} < Ce^{3+}$
(d) $Pm^{3+} < La^{3+} < Ce^{3+} < Yb^{3+}$

25. A solid is made of two elements *X* and *Z*. The atoms *Z* are in *ccp* arrangement while the atom *X* occupy all the tetrahedral sites. What is the formula of the compound?
(a) *XZ* (b) XZ_2
(c) X_2Z (d) X_2Z_3

26. 

(a)  (b)
(c)  (d) 

27. When 0.1 mol $CoCl_3(NH_3)_5$ is treated with excess of $AgNO_3$, 0.2 mol of AgCl are obtained. The conductivity of solution will correspond to
(a) 1 : 3 electrolyte (b) 1 : 2 electrolyte
(c) 1 : 1 electrolyte (d) 3 : 1 electrolyte

28. PHBV is an example of
(a) polysaccharide (b) polyol
(c) polyamide (d) polyester

29. $(CH_3)_2SiCl_2$ on hydrolysis will produce
(a) $(CH_3)_2Si(OH)_2$
(b) $(CH_3)_2Si=O$
(c) $-O\!+\!(CH_3)_2Si\!-\!O\!+_n$
(d) $(CH_3)_2SiCl(OH)$

30. Given $\Lambda^\circ\left(\frac{1}{3}Al^{3+}\right) = 63\ \Omega^{-1}\ cm^2\ mol^{-1}$ and $\Lambda^\circ\left(\frac{1}{2}SO_4^{2-}\right) = 80\ \Omega^{-1}\ cm^2\ mol^{-1}$. The value of $\Lambda^\infty[Al_2(SO_4)_3]$ would be (in $\Omega^{-1}\ cm^2\ mol^{-1}$)
(a) 143 (b) 206
(c) 286 (d) 858

31. At 20°C, the Ag^+ ion concentration in a saturated solution of Ag_2CrO_4 is 1.5×10^{-4} mol/L. At 20°C, the solubility product of Ag_2CrO_4 would be
(a) 3.3750×10^{-12} (b) 1.6875×10^{-10}
(c) 1.6875×10^{-12} (d) 1.6875×10^{-11}

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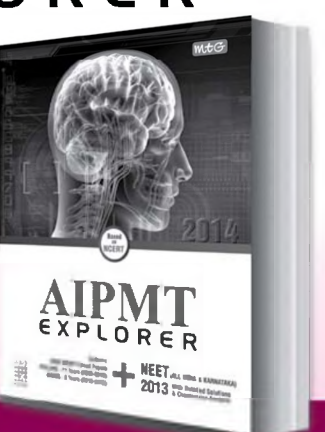

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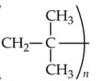
32. 

is a polymer having monomer units

(a) (b)

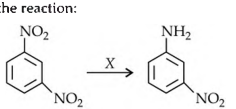
(c) (d)

33. The correct decreasing order of acidic character is
(a) HClO > HBrO > HIO
(b) HIO > HBrO > HClO
(c) HBrO > HIO > HClO
(d) HClO > HIO > HBrO

34. A real gas most closely approaches the behaviour of an ideal gas at
(a) 15 atm and 200 K (b) 1 atm and 273 K
(c) 0.5 atm and 500 K (d) 15 atm and 500 K.

35. The volume of carbon dioxide gas evolved at S.T.P. by heating 7.3 g of $Mg(HCO_3)_2$ will be
(a) 2240 mL (b) 1120 mL
(c) 2340 mL (d) 2000 mL

36. In the reaction:



X is
(a) $(NH_4)_2S$ (b) Zn/NaOH
(c) Zn/NH_4Cl, H_2O (d) Na_3AsO_3/NaOH

37. A solution of (+)-2-chloro-2-phenylethane in toluene racemises slowly in the presence of a small amount of $SbCl_5$, due to the formation of
(a) carbanion (b) carbene
(c) free radical (d) carbocation.

38. The bond lengths of H_2^+, H_2^- and H_2 are in the order
(a) $H_2^+ > H_2 > H_2^-$ (b) $H_2 > H_2^- > H_2^+$
(c) $H_2^- > H_2 > H_2^+$ (d) $H_2^- > H_2^+ > H_2$

39. Phenol associates in benzene to a certain extent to form dimer. A solution containing 2.0×10^{-2} kg of phenol in 1.0 kg of benzene has its freezing point decreased by 0.69 K. The degree of association of phenol is
(K_f for benzene = 5.12 K kg mol^{-1})
(a) 73.4% (b) 50.1%
(c) 42.3% (d) 25.1%

40. Correct IUPAC name of the given compound is

$CH_3C(CH_3)CH_2COOH$

(a) 3-methyl-3-cyclopentylbutanoic acid
(b) 2-methyl-2-cyclopentylbutanoic acid
(c) 1,1-dimethyl-1-cyclopentylethanoic acid
(d) 2-methyl-3-cyclopentylbutanoic acid.

41. A bulb emits light of $\lambda = 4500$ Å. The bulb is rated 150 W and 8% energy is emitted light. The number of photons emitted per second is
(a) 27.2×10^{18} (b) 29.4×10^{2}
(c) 27.2×10^{6} (d) 2.72×10^{9}

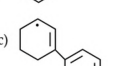
42. When aluminium is heated in atmosphere of nitrogen it forms a nitride of formula
(a) AlN (b) Al_3N
(c) AlN_3 (d) Al_2N_3

43. The emf of the three galvanic cells are represented by E_1, E_2 and E_3.
I. $Zn \mid Zn^{2+}$ (1 M) || Cu^{2+} (1 M) | Cu
II. $Zn \mid Zn^{2+}$ (0.1 M) || Cu^{2+} (1 M) | Cu
III. $Zn \mid Zn^{2+}$ (1 M) || Cu^{2+} (0.1 M) | Cu
Which of the following is true?
(a) $E_1 > E_2 > E_3$ (b) $E_3 > E_2 > E_1$
(c) $E_3 > E_1 > E_2$ (d) $E_2 > E_1 > E_3$

44. Which of the following molecules is the most polar?
(a) CH_3NH_2 (b) $(CH_3)_3CCl$
(c) CH_3NO_2 (d) $(CH_3)_3CH$

45. Most stable free radical is

(a) (b)

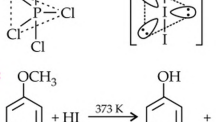
(c)  (d)

SOLUTIONS

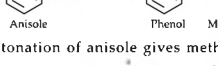
1. (c) : $\alpha = \frac{\Lambda_m}{\Lambda_m^\circ} = \frac{184.5}{502.4} = 0.367$

$$K = \frac{C\alpha^2}{1-\alpha} = \frac{0.001\,M \times (0.367)^2}{0.633}$$
$$= 2.127 \times 10^{-4}\ M$$

2. **(d)**: Both PCl_5 and I_3^- have trigonal bipyramidal geometry.



3. **(b)**:



Anisole Phenol Methyl iodide

Protonation of anisole gives methyl phenyl oxonium ion, $C_6H_5-\overset{+}{\underset{H}{O}}-CH_3$. In this ion, the bond between $O-CH_3$ is weaker than the bond between $O-C_6H_5$ which has partial double bond character due to resonance between the lone pair of electrons on the O atom and the sp^2-hybridised carbon atom of the phenyl group. Therefore, attack by I^- ion breaks the weaker $O-CH_3$ bond forming methyl iodide and phenol.

4. **(d)**: $3B_2H_6 + 6NH_3 \longrightarrow 3[BH_2(NH_3)_2]^+ [BH_4]^- \xrightarrow{\Delta} \underset{\text{Borazine}}{2B_3N_3H_6} + 12H_2$

5. **(b)**: $\underset{\text{(dilute)}}{4Zn + 10HNO_3} \longrightarrow 4Zn(NO_3)_2 + NH_4NO_3 + 3H_2O$

6. **(b)**: $2KMnO_4 + 8H_2SO_4 + 10FeSO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O$

One mole of $KMnO_4$ oxidises five moles of $FeSO_4$ *i.e.* 1 M $KMnO_4$ can oxidise equal amount of 5 M $FeSO_4$.

7. **(a)**: $\rho = \frac{Z \times M}{a^3 \times N_A} \Rightarrow 9.5 = \frac{1 \times 300}{a^3 \times 6.02 \times 10^{23}}$

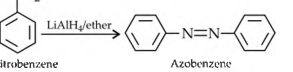
or $a^3 = 5.245 \times 10^{-23} \Rightarrow a = 3.74 \times 10^{-8}$ cm

For simple cubic, $r = \frac{a}{2} = 1.87 \times 10^{-8}$ cm

8. **(d)**: Both NH_4^+ and SO_4^{2-} have tetrahedral shape showing sp^3 hybridisation.

9. **(b)**: BF_3 has a symmetrical trigonal planar structure, hence it has zero dipole moment.

10. **(c)** : Aromatic nitro compounds on reduction with $LiAlH_4$ give azo compounds and not primary amines.



Nitrobenzene Azobenzene

11. **(c)** : $N_2^+ = KK\,(\sigma 2s)^2, (\sigma^*2s)^2, (\pi 2p_x^2 = \pi 2p_y^2), (\sigma 2p_z)^1$

$O_2 = KK\,(\sigma 2s)^2, (\sigma^*2s)^2, (\sigma 2p_z)^2, (\pi 2p_x^2 = \pi 2p_y^2), (\pi^*2p_x^1 = \pi^*2p_y^1)$

$O_2^{2-} = KK\,(\sigma 2s)^2, (\sigma^*2s)^2, (\sigma 2p_z)^2, (\pi 2p_x^2 = \pi 2p_y^2), (\pi^*2p_x^2 = \pi^*2p_y^2)$

$B_2 = KK\,(\sigma 2s)^2, (\sigma^*2s)^2, (\pi 2p_x^1 = \pi 2p_y^1)$

Thus, O_2^{2-} has no unpaired electrons.

12. **(b)**: Metamerism is due to presence of different alkyl groups attached to the same polyvalent functional group or atom.
∴ This kind of isomerism is not possible in case of alkenes.

13. **(a)** : One set of quantum numbers is only for one orbital. In an atom, the two electrons in the same orbital can have the same set of three quantum numbers with a different value for spin quantum number.

14. **(d)**: $E \propto \frac{1}{n^2}$ *i.e.*, when $n = 3$; E decreases nine times.

15. **(b)**: When an alkali is added to dichromate solution then chromate salt formation takes place.

$Cr_2O_7^{2-} + OH^- \longrightarrow 2CrO_4^{2-} + H_2O$

16. **(d)**

17. **(a)** : 6% increase in rate constant, thus

$k_2 = 1.06k_1$

$\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left(\frac{T_2 - T_1}{T_1T_2}\right)$

$\log\frac{1.06}{1} = \frac{E_a}{2.303 \times 8.314}\left(\frac{1}{300 \times 301}\right)$

$= 43.7$ kJ/mol

18. **(a)** : Initially, partial pressures were equal. Now $r \propto \sqrt{1/d}$ or $\sqrt{1/M}$, therefore amounts diffused out in the same time will be $H_2 > CH_4 > SO_2$.
Amounts left will be $H_2 < CH_4 < SO_2$
∴ $p_{SO_2} > p_{CH_4} > p_{H_2}$

19. **(b)**: Spin only magnetic moment, $\mu_s = \sqrt{n(n+2)}$ where, n = number of unpaired electrons.
Number of unpaired electrons in $Cr^{2+}([Ar]\,3d^4)$ is 4, in $Co^{2+}([Ar]\,3d^7)$ is 3, in $Fe^{2+}([Ar]\,3d^6)$ is 4, in $Mn^{2+}([Ar]\,3d^5)$ is 5.

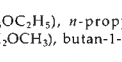
As the number of unpaired electrons in Cr^{2+} and Fe^{2+} is same, hence $[Cr(H_2O)_6]^{2+}$ and $[Fe(H_2O)_6]^{2+}$ will have same magnetic moment.

20. **(a)** : $2H_2S + \underset{\text{Oxidising agent}}{SO_2} \longrightarrow 2H_2O + 3S$

21. **(b)**: Aromaticity can be predicted by the use of Huckle's rule which says that $(4n + 2)$ π-electrons are required in delocalisation system to give it aromaticity.
$(4n + 2)\pi$ electrons means 2, 6, 10 .....π electrons.

Here total number of electrons available for delocalisation is 6. Therefore, it is expected to be aromatic.

22. **(d)**: Diethyl ether $(C_2H_5OC_2H_5)$, *n*-propyl methyl ether $(CH_3CH_2CH_2OCH_3)$, butan-1-ol $(CH_3CH_2CH_2CH_2OH)$,

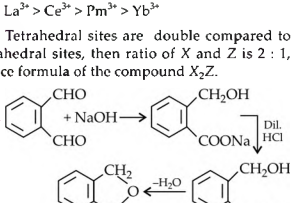
2-methylpropan-2-ol  all have

molecular formula $C_4H_{10}O$, hence these are isomeric with diethyl ether. The molecular formula of butan-2-one $(CH_3CH_2COCH_3)$ is different, it is C_4H_8O. So it is not isomeric with diethyl ether.

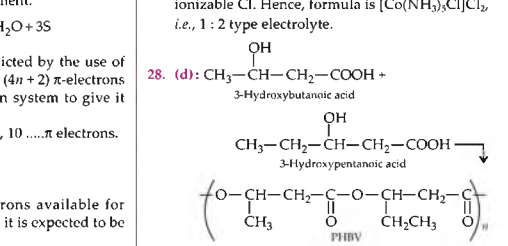
23. **(a)** : Essential condition for tautomerism is the presence of an α-hydrogen on a saturated carbon attached to C = O, NO, NO_2, etc. or should have a H-atom present on a heteroatom (O, N, S, etc.) attached to a double bond. Thus, option (a) does not have α-hydrogen on a saturated carbon and hence does not exhibit tautomerism.

24. **(a)** : Ionic radii of lanthanoids decrease across the series due to lanthanoid contraction. Thus, order of ionic radii is
$La^{3+} > Ce^{3+} > Pm^{3+} > Yb^{3+}$

25. **(c)** : Tetrahedral sites are double compared to octahedral sites, then ratio of *X* and *Z* is 2 : 1, hence formula of the compound X_2Z.

26. **(b)**: 

27. **(b)**: Formation of 0.2 mol of AgCl from 0.1 mol of the complex means that there are two ionizable Cl. Hence, formula is $[Co(NH_3)_5Cl]Cl_2$, *i.e.*, 1 : 2 type electrolyte.

28. **(d)**: 

29. **(c)** : Due to very large size of Si atom than that of oxygen atom, it fails to form a π-bond and so the product of hydrolysis of $(CH_3)_2SiCl_2$ is a polymer *i.e.* $-O\text{-}(CH_3)_2Si\text{-}O\text{-}]_n$

30. **(d)**: $\Lambda°(Al^{3+}) = 3\Lambda°\left(\frac{1}{3}Al^{3+}\right)$

$= 3 \times 63 = 189\ \Omega^{-1}\ cm^2\ mol^{-1}$

$\Lambda°\left(SO_4^{2-}\right) = 2\Lambda°\left(\frac{1}{2}SO_4^{2-}\right)$

$= 2 \times 80 = 160\ \Omega^{-1}\ cm^2\ mol^{-1}$

$\Lambda°[Al_2(SO_4)_3] = 2\ \Lambda°(Al^{3+}) + 3\Lambda°\left(SO_4^{2-}\right)$

$= 2 \times 189 + 3 \times 160 = 858\ \Omega^{-1}\ cm^2\ mol^{-1}$

31. **(c)** : $\underset{2S}{Ag_2CrO_4} \rightleftharpoons \underset{2S}{2Ag^+} + \underset{S}{CrO_4^{2-}}$

$\therefore\ K_{sp} = [Ag^+]^2[CrO_4^{2-}] = (2S)^2 \times S$

$= (1.5\times10^{-4})^2 \times \left(\frac{1.5\times10^{-4}}{2}\right)$ $[\because 2S = 1.5 \times 10^{-4}]$

$= 1.6875 \times 10^{-12}$

32. **(a)** : $n\underset{\text{Isobutylene}}{CH_2{=}C(CH_3){-}CH_3} \longrightarrow \left(CH_2{-}\underset{CH_3}{\overset{CH_3}{C}}\right)_n$

33. **(a)** : Acidity decreases as the electronegativity of the central halogen decreases from Cl to I in HXO.

34. **(c)** : A real gas approaches the behaviour of ideal gas when the pressure is low and the temperature is high.

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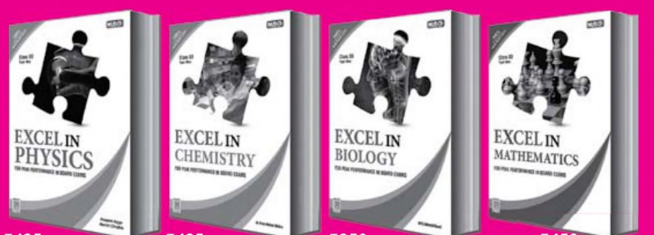

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35. **(a)** : $Mg(HCO_3)_2 \rightarrow MgO + 2CO_2 + H_2O$

146 g of $Mg(HCO_3)_2$ gives 22.4 × 2 litre of CO_2

$\Rightarrow$ 7.3 g of $Mg(HCO_3)_2$ will give $\frac{22.4}{146} \times 7.3 \times 2$

$= 2.24$ L of CO_2

$= 2240$ mL of CO_2

36. **(a)** : Reduction of *m*-dinitrobenzene with sodium or ammonium sulphide gives *m*-nitroaniline.

37. **(d)**: 2-Chloro-2-phenylethane racemises *i.e.*, it proceeds *via* the formation of carbocation.

38. **(d)**: Bond order in $H_2 = \frac{1}{2}(2-0) = 1$

B.O. in $H_2^+ = \frac{1}{2}(1-0) = \frac{1}{2}$

B.O. in $H_2^- = \frac{1}{2}(2-1) = \frac{1}{2}$

Although H_2^+ and H_2^- have the same bond order, H_2^- has longer bond length than H_2^+ because of the presence of one electron in the anti-bonding orbital which repels the two H-atoms from coming close.

Further because of larger B.O., H_2 molecule has the shortest bond length. Thus, the actual order of bond length is $H_2^- > H_2^+ > H_2$.

39. **(a)** : $M_2(\text{obs}) = \frac{K_f \times w \times 1000}{W \times \Delta T_f}$

$= \frac{5.12 \times 2.0 \times 10^{-2} \times 1000}{1.0 \times 0.69} = 148.4$

Calculated molecular mass of phenol = 94

$i = \frac{M_2(\text{cal})}{M_2(\text{obs})} = \frac{94}{148.4} = 0.633$

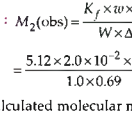
$2C_6H_5OH \underset{1-\alpha}{\rightleftharpoons} \underset{\alpha/2}{(C_6H_5OH)_2}$

Total species $= (1-\alpha) + \frac{\alpha}{2} = 1 - \frac{\alpha}{2}$

$i = \frac{1-\alpha/2}{1}$ or $\frac{\alpha}{2} = 1 - i$

or $\alpha = 2(1-i) = 2(1-0.633) = 0.734 = 73.4\%$

40. **(a)** :



3-Methyl-3-cyclopentylbutanoic acid

41. **(a)** : Energy of one photon,

$h\nu = \frac{hc}{\lambda} = \frac{6.62 \times 10^{-34} \times 3 \times 10^8}{4500 \times 10^{-10}}$

$= 4.42 \times 10^{-19}$ J

Energy emitted by bulb = 8% of 150 watt

$= \frac{8 \times 150}{100} = 12$ J

No. of photons $= \frac{12}{4.42 \times 10^{-19}} = 27.2 \times 10^{18}$

42. **(a)** : Aluminium when heated with nitrogen forms aluminium nitride.

$2Al + N_2 \longrightarrow 2AlN$

43. **(d)**: $E_{cell} = E^\circ_{cell} - \frac{RT}{nF} \ln \frac{[Zn^{2+}]}{[Cu^{2+}]}$

In first case $\frac{[Zn^{2+}]}{[Cu^{2+}]} = 1$ thus $E_{cell} = E^\circ_{cell}$

In second case $\frac{[Zn^{2+}]}{[Cu^{2+}]} = \frac{0.1}{1}$

$\therefore \quad E_{cell} = E^\circ_{cell} - \frac{0.0591}{n} \log 10^{-1}$

$= E^\circ_{cell} + \frac{0.0591}{n}$

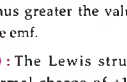
In third case $\frac{[Zn^{2+}]}{[Cu^{2+}]} = \frac{1}{0.1} = 10$

$\therefore \quad E_{cell} = E^\circ_{cell} - \frac{0.0591}{n} \log 10 = E^\circ_{cell} - \frac{0.0591}{n}$

Therefore $E_2 > E_1 > E_3$

Thus greater the value of $[Zn^{2+}]/[Cu^{2+}]$, less is the emf.

44. **(c)** : The Lewis structure of CH_3NO_2 has a formal charge of +1 on nitrogen, making it more electron attracting than the other structures.



45. **(c)** : The free radical (c) is stabilised by resonance due to the presence of phenyl group as a substituent.

■■

NCERT Xtract

New

Questions for Medical/ Engineering Entrance Exams

Haloalkanes and Haloarenes | Alcohols, Phenols and Ethers | Aldehydes, Ketones and Carboxylic Acids | Amines

1. Which of the isomeric C_4H_9Cl compounds will be optically active?

(a) $CH_3CH_2CH_2CH_2Cl$ (b) $CH_3CH_2\underset{\underset{Cl}{|}}{CH}-CH_3$

(c) $H_3C-\underset{\underset{Cl}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$ (d) $H_3C-\underset{\underset{CH_3}{|}}{CH}-CH_2Cl$

2. The relative ease of dehydration of following alcohols is

$\underset{I}{CH_3CH(OH)CH_3}$, $\underset{II}{(CH_3)_3COH}$, $\underset{III}{CH_3CH_2CH_2OH}$

(a) I > II > III (b) III > I > II
(c) III > II > I (d) II > I > III

3. Which of the following alcohols will yield the corresponding alkyl chloride on reaction with concentrated HCl at room temperature?

(a) $CH_3CH_2CH_2OH$

(b) $CH_3CH_2-\underset{\underset{CH_3}{|}}{CH}-OH$

(c) $CH_3CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_2OH$

(d) $CH_3CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-OH$

4. The correct order of decreasing strength of the following acids is

(a) $C_6H_5SO_3H > C_6H_5COOH > C_6H_5CH_2COOH > C_6H_5OH$
(b) $C_6H_5SO_3H > C_6H_5COOH > C_6H_5OH > C_6H_5CH_2COOH$
(c) $C_6H_5CH_2COOH > C_6H_5COOH > C_6H_5OH > C_6H_5SO_3H$
(d) $C_6H_5OH > C_6H_5CH_2COOH > C_6H_5COOH > C_6H_5SO_3H$

5. In which of the following halides, the halogen atom is attached to sp^3 hybridised carbon atom?

(a) Allylic halides (b) Vinylic halides
(c) Benzylic halides (d) Both (a) and (c)

6. Correct arrangement of the following acids in decreasing order of pK_a values is

$\underset{I}{CH_3COOH}$, $\underset{II}{Cl_2CHCOOH}$, $\underset{III}{F_3CCOOH}$, $\underset{IV}{ClCH_2COOH}$, $\underset{V}{FCH_2COOH}$

(a) I > III > II > IV > V (b) I > IV > V > II > III
(c) III > II > I > V > IV (d) II > III > I > IV > V

7. Arrange the following $CH_3CH_2CH_2Cl$ (I), $CH_3CH_2CH(Cl)CH_3$ (II), $(CH_3)_2CHCH_2Cl$ (III) and $(CH_3)_3CCl$ (IV) in order of decreasing tendency towards S_N2 reaction.

(a) I > III > II > IV (b) III > IV > II > I
(c) II > I > III > IV (d) IV > III > II > I

8. Which one of the following reaction is a method for the conversion of a ketone into a hydrocarbon?

(a) Aldol condensation
(b) Reimer–Tiemann reaction
(c) Cannizzaro reaction
(d) Wolff–Kishner reduction

9. Amongst the following, the most basic compound is
   (a) benzylamine (b) aniline
   (c) acetanilide (d) *p*-nitroaniline

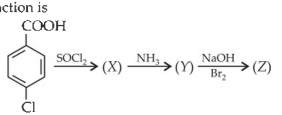
10. The reagent which does not react with both acetone and benzaldehyde is
   (a) sodium hydrogensulphite
   (b) phenylhydrazine
   (c) Fehling's solution (d) Grignard's reagent

11. Hinsberg's reagent is
   (a) aliphatic sulphonyl chloride
   (b) phthalimide
   (c) aromatic sulphonyl chloride
   (d) anhydrous $ZnCl_2$ + conc. HCl.

12. Which of the following does not undergo HVZ reaction?
   (a) CH_3CH_2COOH (b) $CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle |}{CH}}-COOH$
   (c) $CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}-COOH$ (d) None of these.

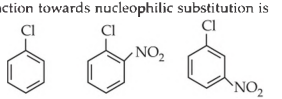
13. Which of the following is least acidic?
   (a) *p*-Nitrobenzoic acid
   (b) Benzoic acid
   (c) *p*-Hydroxybenzoic acid
   (d) *p*-Methylbenzoic acid

14. The product (Z) of the following sequence of reaction is



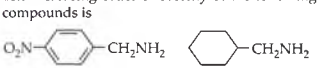
   (a) *p*-chlorobenzamide (b) *p*-chlorobenzene
   (c) *p*-chlorotoluene (d) *p*-chloroaniline

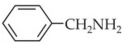
15. The compounds in increasing order of rate of reaction towards nucleophilic substitution is



   (a) I < II < III (b) III < II < I
   (c) I < III < II (d) III < I < II

16. The increasing order of basicity of the following compounds is





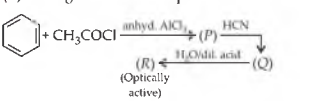
   (a) I < III < II (b) I < II < III
   (c) III < II < I (d) III < I < II

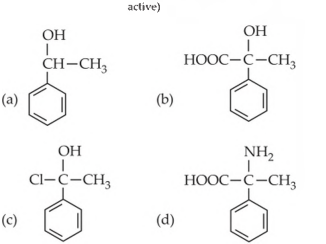
17. The final product of the following reaction is
   $CH_3CH=CHCH_2OH \xrightarrow{PCC}$
   (a) $CH_3CH=CHCHO$
   (b) $CH_3CH_2CH_2CHO$
   (c) $CH_3CH=CHCOOH$
   (d) $CH_3CH_2CH_2COOH$

18. Picric acid is
   (a) 2,4,6-trinitrophenol
   (b) 1,3,5-tribromobenzene
   (c) 2,4,6-tribromophenol
   (d) 1,3,5-trinitrobenzene

19. Primary and secondary amines are distinguished by
   (a) Br_2/KOH (b) HClO
   (c) HNO_2 (d) NH_3

20. (*R*) in the given reaction sequence is





21.

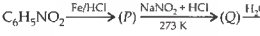
   Major and minor products are respectively
   (a) *p*-bromophenol, *m*-bromophenol
   (b) *o*-bromophenol, *p*-bromophenol
   (c) *p*-bromophenol, *o*-bromophenol
   (d) *o*-bromophenol, *m*-bromophenol.

22. The compound which reacts fastest with Lucas reagent at room temperature is
(a) butan-1-ol (b) butan-2-ol
(c) 2-methylpropan-1-ol
(d) 2-methylpropan-2-ol

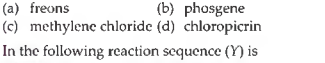
23. Out of the following, which is incorrect resonating structure of diazonium salt?
(a)
(b)
(c)
(d)

24. (*R*) in the given reaction sequence is
$C_6H_5NO_2 \xrightarrow{Fe/HCl} (P) \xrightarrow[273\ K]{NaNO_2 + HCl} (Q) \xrightarrow[\Delta]{H_2O/H^+} (R)$
(a) $C_6H_5NH_2$ (b) C_6H_5OH
(c) C_6H_5COOH (d) $C_6H_5CONH_2$

25. Chloroform is slowly oxidised by air in the presence of light to an extremely poisonous gas known as
(a) freons (b) phosgene
(c) methylene chloride (d) chloropicrin

26. In the following reaction sequence (*Y*) is

(a) benzene (b) phenol
(c) aniline (d) cyclohexane

27. Acetophenone on Wolff–Kishner reduction gives
(a) benzophenone (b) acetic acid
(c) acetone (d) ethylbenzene.

28. In the following sequence of reactions (Z) is

(a)
(b)
(c)
(d)

29. Which of the following does not contain a carboxyl group?
(a) Picric acid (b) Aspirin
(c) Benzoic acid (d) Ethanoic acid

30. The final product of the following reaction is
$CH_3CH_2OH \xrightarrow[573\ K]{Cu} \xrightarrow[(ii)\ H_2O/H^+]{(i)\ CH_3MgBr} \xrightarrow[573\ K]{Cu}$
(a) acetaldehyde (b) acetic acid
(c) acetone (d) acetophenone.

31. Aldol condensation is a characteristic reaction of
(a) all aldehydes and ketones
(b) only those aldehydes and ketones which contain α-hydrogen atoms
(c) only those aldehydes and ketones which do not contain α-hydrogen atoms
(d) only aromatic aldehydes and ketones.

32. The correct order of decreasing basicity of the given amines in gaseous phase is

CH_3NH_2	NH_3	$(CH_3)_2NH$	$(CH_3)_3N$
I	II	III	IV

(a) I > II > III > IV (b) III > II > IV > I
(c) III > I > II > IV (d) IV > III > I > II

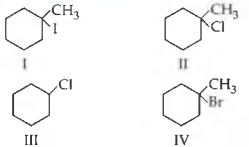
33. Which of the following compounds has the highest boiling point?
(a) $CH_3CH_2CH_2Cl$
(b) $CH_3CH_2CH_2CH_2Cl$
(c) $CH_3CH(CH_3)CH_2Cl$
(d) $(CH_3)_3CCl$

34. The correct set of compounds in order of increasing boiling points is
(I) Bromoform (II) Dibromomethane
(III) Bromomethane (IV) Chloromethane
(V) Dichloromethane
(a) I < II < III < V < IV
(b) IV < V < III < II < I
(c) V < IV < I < III < II
(d) II < I < III < IV < V

35. Which of the following is 3° amine?
(a)
(b)
(c)
(d)

HIGHER ORDER THINKING SKILLS QUESTIONS (HOTS)

36. The increasing order of reactivity of the following compounds in S_N1 reaction is



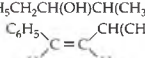
(a) III < II < IV < I (b) IV < III < II < I
(c) I < II < III < IV (d) II < I < IV < III

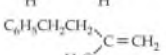
37. An organic compound 'X' on treatment with NH_3 gives 'Y' which on heating gives 'Z'. 'Z' when treated with Br_2 in the presence of KOH produces ethylamine. Compound 'X' is

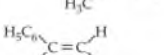
(a) CH_3COOH (b) $CH_3CH_2CH_2COOH$
(c) $CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}HCOOH$ (d) CH_3CH_2COOH

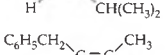
38. The main product of the following reaction is

$C_6H_5CH_2CH(OH)CH(CH_3)_2 \xrightarrow{\text{conc. } H_2SO_4} ?$

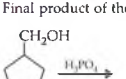
(a) 

(b) 

(c) 

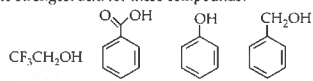
(d) 

39. Final product of the following reaction is



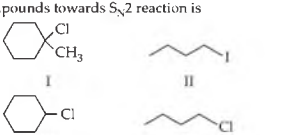
(a) (b) (c) (d)

40. What is the correct order of acidity from weakest to strongest acid for these compounds?



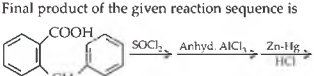
(a) I < IV < III < II (b) III < IV < I < II
(c) IV < I < III < II (d) II < III < I < IV

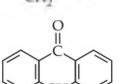
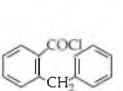
41. Increasing order of reactivity of the following compounds towards S_N2 reaction is

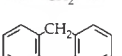
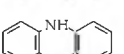


(a) I < II < III < IV (b) IV < III < II < I
(c) I < III < IV < II (d) III < II < IV < I

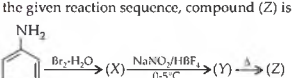
42. Final product of the given reaction sequence is



(a)  (b) 

(c)  (d) 

43. In the given reaction sequence, compound (Z) is



(a) 2,4,6-tribromoaniline
(b) picric acid
(c) 2,4,6-tribromophenol
(d) 2,4,6-tribromofluorobenzene

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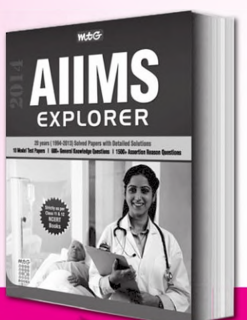

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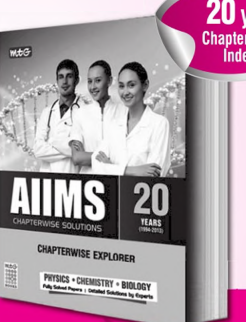

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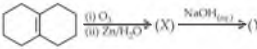
44. In the given reaction sequence (*Y*) is



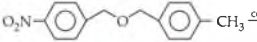
(a)

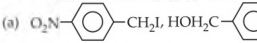
(b)

(c)

(d)

45. What is the product of the given reaction?



(a) 

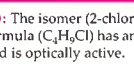
(b)

(c)

(d) No reaction

SOLUTIONS

1. **(b)**: The isomer (2-chlorobutane) of the molecular formula (C_4H_9Cl) has an asymmetric carbon atom and is optically active.



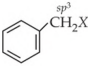
The centre carbon atom has four different groups or atoms.

2. **(d)**: The relative ease of dehydration of alcohols follows the order 3° > 2° > 1°.

3. **(d)**: Tertiary alcohol will yield the corresponding alkyl chloride on reaction with concentrated HCl at room temperature because it is most reactive.

4. **(a)**: Greater the *–I* effect, more will be the acidic strength. The order of *–I* effect is $-SO_3H > -COOH > -OH$

5. **(d)**: Allylic halides:

Benzylic halides : 

Vinylic halides :

6. **(b)**: More the electron withdrawing effect, the compound will be more acidic. More the number of halogen atoms, greater would be the dispersion of the negative charge. Hence more will be stabilisation of anion and the compound will be more acidic. More the value of pK_a, less acidic will be the compound. Smaller the value of pK_a, the compound will be more acidic.

7. **(a)**: In the S_N2 reaction, there will be crowding in the transition state. Bulkier the groups, greater the steric effect and hence reaction will be more hindered.

8. **(d)**:

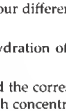
9. **(a)**:

In benzylamine, electron pair on nitrogen is not delocalised due to lack of conjugation. While in all other compounds it is delocalised, hence less available for protonation.

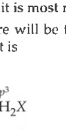
10. **(c)** **11.** **(c)**

12. **(c)** : For HVZ reaction, the carboxylic acids must have atleast one α-hydrogen atom.

13. **(c)** : If substituent is electron releasing group ($-CH_3$), then acidic strength is decreased while acidity increases with the presence of electron withdrawing group ($-NO_2$).



14. **(d)**:



p-Chloroaniline

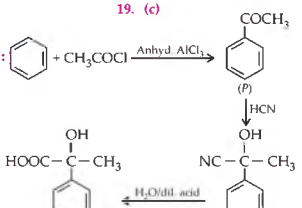
15. **(c)** : An electron withdrawing group increases the reactivity towards nucleophilic substitution reaction. The effect is more at *ortho*-position than at *meta*-position.

16. (a): In (II), the β-carbon in ring uses sp^3 hybrid orbitals. In (III), the β-carbon uses sp^2 hybrid orbitals. However, in (I), presence of electron withdrawing group ($-NO_2$) enhances the electron withdrawal by the ring which further weakens the base.

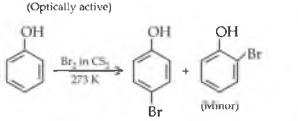
17. (a): $CH_3CH{=}CHCH_2OH \xrightarrow{PCC} CH_3CH{=}CHCHO$

18. (a) **19. (c)**

20. (b):

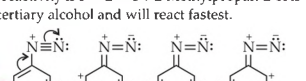


21. (c):



22. (d): By Lucas test we can distinguish between primary, secondary and tertiary alcohols. On reaction with Lucas reagent (conc. HCl and anhyd. $ZnCl_2$) at room temperature, *tert.* alcohols (3°) produce turbidity immediately, secondary alcohols (2°) give turbidity in 5-10 minutes, primary alcohols (1°) remain clear, *i.e.*, the order of reactivity is 3° > 2° > 1°. 2-Methylpropan-2-ol is a tertiary alcohol and will react fastest.

23. (c):

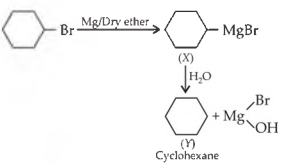


24. (b): $C_6H_5NO_2 \xrightarrow{Fe/HCl} C_6H_5NH_2$ (P)

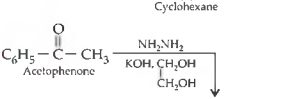
$C_6H_5NH_2 \xrightarrow[273\ K]{NaNO_2 + HCl} C_6H_5N_2^+Cl^- \xrightarrow[\Delta]{H_2O/H^+} C_6H_5OH$ (R) (Q)

25. (b): $2CHCl_3 + O_2 \xrightarrow{light} \underset{\text{Phosgene}}{2COCl_2} + 2HCl$

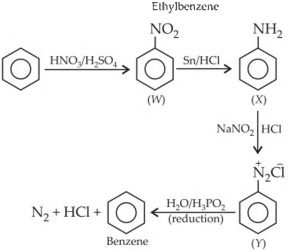
26. (d):



27. (d):

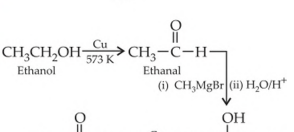


28. (b):



29. (a)

30. (c):



31. (b)

32. (d): In gaseous phase, the basicity of amines depends only on the *+I* effect of the alkyl groups. More is the *+I* effect, more is the basicity.
Thus, the basicity of amines decreases in the order:
3° amine > 2° amine > 1° amine > ammonia

33. (b): For the same halogen, boiling point of alkyl halide decreases as the size of the alkyl group decreases.
For isomeric alkyl halides, boiling point decreases as branching increases. So, the decreasing order of boiling point is
$CH_3CH_2CH_2CH_2Cl > CH_3CH_2CH_2Cl > CH_3CH(CH_3)CH_2Cl > (CH_3)_3CCl$

34. (b): For the same alkyl group, boiling point increases with the increase in the size of the halogen atom. The boiling point increases as the number of halogen atoms increases.
The increasing order of boiling points of the given compounds is

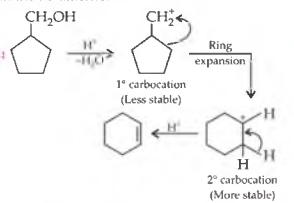
IV < V < III < II < I

35. (b)

36. (a): Compounds (I), (II) and (IV) are 3° alkyl halides while compound (III) is 2° alkyl halide.
Since 3° alkyl halides are more reactive than 2° alkyl halides towards S_N1 reaction, compound (III) is least reactive. Further reactivity increases in the order chloride < bromide < iodide (better leaving group). Thus, the increasing order of reactivity in S_N1 reactions is
III < II < IV < I

37. (d): $CH_3CH_2COOH \xrightarrow{NH_3} CH_3CH_2COONH_4$
Propionic acid (X) — Ammonium propanoate (Y)
$CH_3CH_2NH_2 \xleftarrow{Br_2/KOH} CH_3CH_2CONH_2 \xleftarrow[-H_2O]{\Delta}$
Ethylamine — Propanamide (Z)

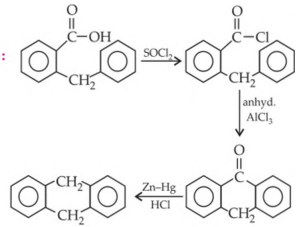
38. (c): Dehydration occurs in such a way that the double bond comes in conjugation with the C_6H_5 group and further *trans*-alkenes are more stable than the *cis*-alkenes.

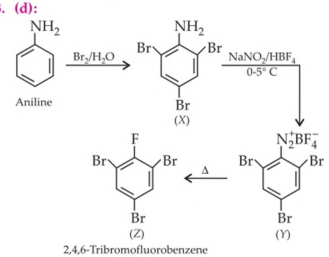
39. (c):


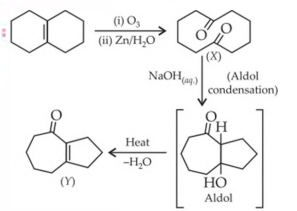
40. (c): Carboxylic acids are stronger acids than phenols and phenols are stronger acids than alcohols. Among alcohols, due to strong $-I$ effect of F atoms, CF_3CH_2OH is a stronger acid than benzyl alcohol. Thus, the overall acidic character increases in the order : IV < I < III < II.

41. (c): The order of reactivity of alkyl halides towards S_N2 reactions is 1° > 2° > 3°. Thus compound (I) being a 3° alkyl halide is least reactive.
Out of 1° alkyl halides (II) and (IV), due to large size and lower electronegativity of I^- ion, it is better leaving group than Cl^- ion, therefore, the correct order of reactivity towards S_N2 reaction is

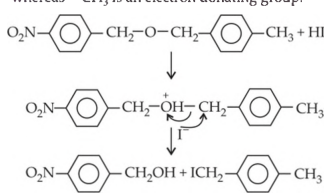
I < III < IV < II

42. (c):


43. (d):


44. (c):


45. (b): $-NO_2$ is an electron withdrawing group, whereas $-CH_3$ is an electron donating group.



YOU ASKED WE ANSWERED

Do you have a question that you just can't get answered?

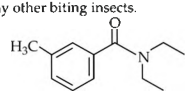
Use the vast expertise of our mtg team to get to the bottom of the question. From the serious to the silly, the controversial to the trivial, the team will tackle the questions, easy and tough.

The best questions and their solutions will be printed in this column each month.

Q1. What chemical is used in mosquito repellent creams?

– Kartik, Lucknow

Ans. *N,N*-Diethyl-*meta*-toluamide, abbreviated as DEET (a slightly yellow coloured oil) is the most common active ingredient in insect repellents. It is intended to be applied to the skin or to clothing, and provides protection against mosquito bites and many other biting insects.



(IUPAC name: *N,N*-Diethyl-3-methylbenzamide)

Advanced Odomos cream contains 12% *N,N*-diethylbenzamide and DEET cream (12% *N, N*-diethyl-3-methylbenzamide).

Q2. What is organic food?

– Suresh Wadhwa, Delhi

Ans. For foods to be labelled as organic, at least 95% of the ingredients must come from organically produced plants and animals. All artificial colourings and sweeteners are banned in organic food. Farmers who grow organic products do not use conventional methods to fertilize, control weeds or prevent livestock disease. For example, rather than using chemical weedkillers, organic farmers may conduct more sophisticated crop rotations and spread mulch or manure to keep weeds at bay.

Q3. Which organic compound is mixed with LPG to detect leakage?

– Mukul, Haryana

Ans. Chemically it is ethanethiol or commonly known as ethyl mercaptan (CH_3CH_2SH). It is toxic in nature and is commonly derived from crude oil. Ethanethiol has a strong bad odour. Ethanethiol is added to butane and propane (LPG) to impart an easily noticed smell to these odourless fuels, that otherwise pose the threat of fire or explosion.

Q4. What do you mean by the term 'food irradiation'?

– Pratima, Ludhiana

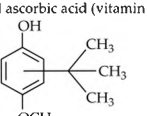
Ans. Food irradiation involves the use of either high-speed electron beams or high-energy radiations with wavelengths smaller than 200 nm, or 2000 Å (*e.g.*, X-rays and γ-rays). These rays contain sufficient energy to break chemical bonds and ionize molecules that lie in their path. The two most common sources of high-energy radiations used in the food industry are cobalt-60 (^{60}Co) and cesium-137 (^{137}Cs). For the same level of energy, γ-rays have a greater penetrating power into foods than high-speed electrons.

The energy from the γ-ray passing through the food is enough to destroy many disease-causing bacteria as well as those that cause food to spoil, but is not strong enough to change the quality, flavour or texture of the food. It is important to keep in mind that the food never comes in contact with the radioisotope and is never at risk of becoming radioactive.

Q5. What chemicals are used in food preservation?

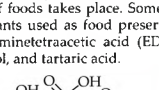
– Mauoj Nair, Gujarat

Ans. Some antioxidants such as BHA (butylated hydroxy-anisole) and BHT (butylated hydroxytoluene) are added to foods to prevent spoilage. Few other examples of food additives are sodium benzoate and benzoic acid, sodium and potassium sulfite, calcium, sodium ascorbate, and ascorbic acid (vitamin C).



(BHA)

A special class of additives that reduce oxidation is known as the sequestrants. Sequestrants are compounds that "capture" metallic ions, such as those of copper, iron and nickel, and remove them from contact with foods. The removal of these ions helps preserve foods because in their free state they increase the rate at which oxidation of foods takes place. Some examples of sequestrants used as food preservatives are ethylenediaminetetraacetic acid (EDTA), citric acid, sorbitol, and tartaric acid.



(Citric acid)

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UNIT-7

Organic Compounds Containing Oxygen | Organic Compounds Containing Nitrogen

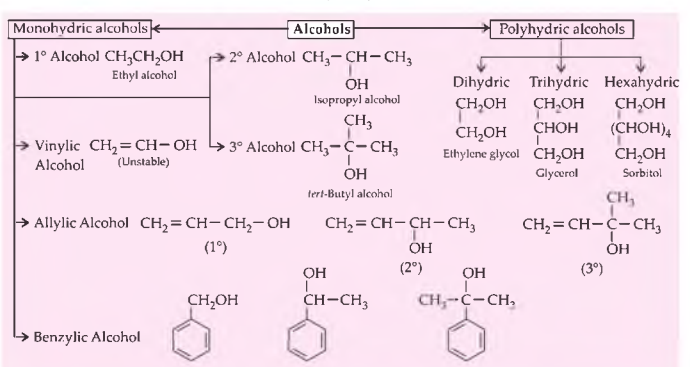
ORGANIC COMPOUNDS CONTAINING OXYGEN

- Introduction
- Classification, Nomenclature, Structure, Preparation, Properties, Distinction, Uses
- Alcohols, Phenols and Ethers
- Aldehydes and Ketones
- Carboxylic Acids

TIPS TO REMEMBER

ALCOHOLS

- **General formula :** Alcohols are the hydroxy derivatives of alkanes having general formula $C_nH_{2n+1}OH$.
- **Classification :** Alcohols are classified as monohydric and polyhydric alcohols depending upon the number of hydroxyl(—OH) groups present in the molecule.

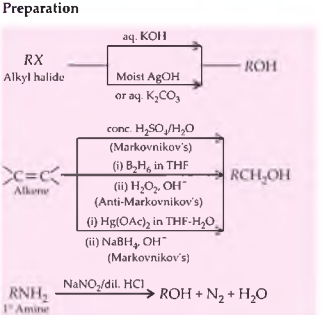


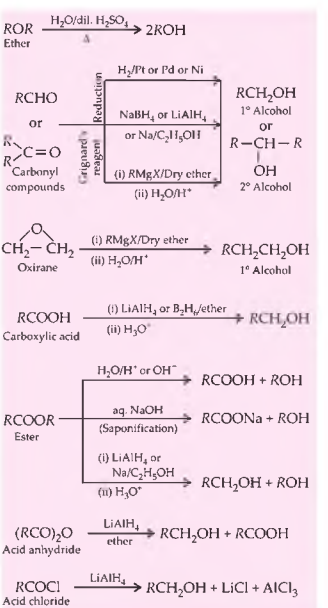
- **Nomenclature :** In common system, alcohols are named as alkyl alcohol.
  - According to IUPAC system, alcohols are called '*alkanols*', by replacing '*-e*' of alkane by '*-ol*'.

Compound	Common name	IUPAC name
$CH_3-CH_2-CH_2-CH_2-OH$	*n*-Butyl alcohol	Butan-1-ol
$CH_3-\underset{\displaystyle OH}{\underset{\vert}{CH}}-CH_2-CH_3$	*sec*-Butyl alcohol	Butan-2-ol
$CH_3-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-CH_2-OH$	Isobutyl alcohol	2-Methylpropan-1-ol
$CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{\vert}{\underset{\vert}{C}}}}-OH$	*tert*-Butyl alcohol	2-Methylpropan-2-ol
$\underset{\displaystyle OH}{\underset{\vert}{CH_2}}-\underset{\displaystyle OH}{\underset{\vert}{CH}}-\underset{\displaystyle OH}{\underset{\vert}{CH_2}}$	Glycerol	Propane -1, 2, 3-triol

- **Structure :** In alcohols, $R-OH$, the O atom of hydroxyl group is attached to C atom by a sigma (σ) bond formed by the overlap of sp^3 hybridised orbital of C atom with sp^3 hybridised orbital of O atom.
  - O atom of the hydroxyl group has two bond pairs and two lone pairs of electrons. The $C-O-H$ bonds are not linear and the bond angle is 108.9°, slightly less than tetrahedral angle (109°28') due to the repulsion between two lone pairs of electrons of O atom.

- **Preparation**





- **Reducing nature of different reagents**

Functional Group	Product	$LiAlH_4$/ Ether	$NaBH_4$/ EtOH	B_2H_6/ THF	H_2/ Metal
$-CHO$	$-CH_2OH$	✓	✓	✓	✓
$>CO$	$>CHOH$	✓	✓	✓	✓
$-COOH$	$-CH_2OH$	✓	×	✓	✓ (with Ru−C)
$-COCl$	$-CH_2OH$	✓	✓	×	✓
$(RCO)_2O$	RCH_2OH	✓	×	✓	✓
$-CO_2R$	$-CH_2OH$	✓	×	✓	✓
$>C=C<$	$>CH-CH<$	×	×	✓	✓

Physical Properties

- **Physical state :** Lower alcohols are colourless liquids with characteristic smell while higher alcohols are colourless, odourless waxy solids.
- **Solubility :** Solubility of alcohols in water is due to their ability to form hydrogen bonds with water molecules.
  - The solubility decreases with increase in size of an alkyl groups.
- **Boiling points :** The boiling points of alcohols increase with increase in the number of carbon atoms as van der Waals forces increase.

Key Points

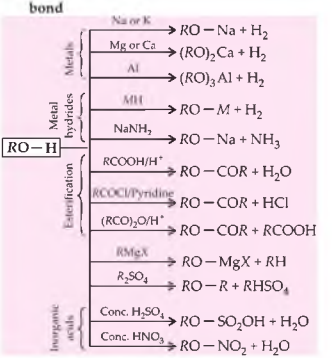
- For isomeric alcohols, solubility increases with increase in branching: 1° < 2° < 3°
- In alcohols, the boiling points decrease with increase of branching in carbon chain due to decrease in van der Waals forces with decrease in surface area.
  1° > 2° > 3°

Chemical Properties

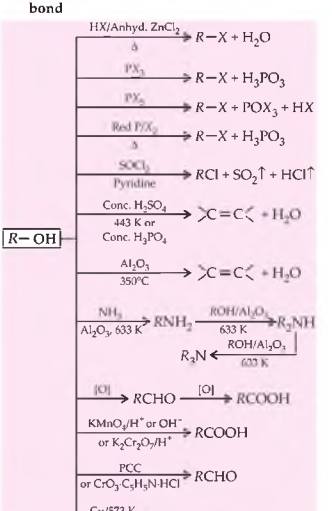
- Alcohols react both as nucleophiles and electrophiles.
  - Alcohols react as nucleophiles when the bond between O − H is broken.
  - Alcohols react as electrophiles when the bond between C − O is broken.

Chemical Reactions

- **Reactions involving cleavage of O − H bond**

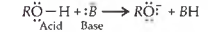


- **Reactions involving cleavage of C − O bond**



Key Points

- Acidity of alcohols : 1° > 2° > 3°
  More the number of electron releasing groups, lesser will be the acidic strength.

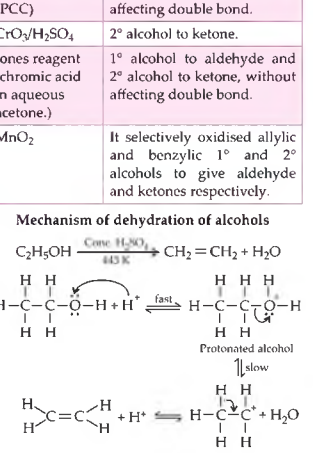


- The order of reactivity of reactions involving cleavage of C — OH bond is
  3° > 2° > 1°
- 3° alcohols do not undergo oxidation reaction, with strong oxidising agents like $KMnO_4$ in neutral or alkaline solution but are readily oxidised in acidic solution ($K_2Cr_2O_7/H_2SO_4$ or $KMnO_4/H_2SO_4$). Cleavage of C — C bond takes place and a mixture of carboxylic acids containing lesser number of carbon atoms is formed.

Oxidising nature of different reagents

Reagent	Purpose
Chromic acid, H_2CrO_4	1° alcohol to carboxylic acid.
Pyridinium chlorochromate (PCC)	1° alcohol to aldehyde and 2° alcohol to ketone without affecting double bond.
CrO_3/H_2SO_4	2° alcohol to ketone.
Jones reagent (chromic acid in aqueous acetone.)	1° alcohol to aldehyde and 2° alcohol to ketone, without affecting double bond.
MnO_2	It selectively oxidised allylic and benzylic 1° and 2° alcohols to give aldehyde and ketones respectively.

Mechanism of dehydration of alcohols



Key Points

- Ease of dehydration of alcohols follow the order of stability of carbocations (as they are formed as an intermediate).
  3° alcohols > 2° alcohols > 1° alcohols
- Dehydration of alcohol always occurs in accordance with the Saytzeff rule *i.e.*, the more substituted alkene is the major product.
- Dehydration of alcohols often give alkenes derived from rearranged carbocations.

Distinction between 1°, 2° and 3° alcohols

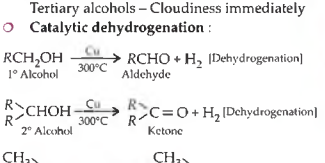
Dichromate test (Oxidation test) :

Primary	Secondary	Tertiary
$R-CH_2OH$	$R^{R'}>CH-OH$	$R^{R'}>C(R'')-OH$
[O] $Na_2Cr_2O_7 + H_2SO_4$	[O] $Na_2Cr_2O_7 + H_2SO_4$	[O] $Na_2Cr_2O_7 + H_2SO_4$
$R-C(=O)-H$ Aldehyde	$R^{R'}>C=O$ Ketone (orange solution becomes green)	No reaction (solution remains orange)
[O] $Na_2Cr_2O_7 + H_2SO_4$		
$R-C(=O)-OH$ Acid (orange solution becomes green)		

Victor Meyer's test :

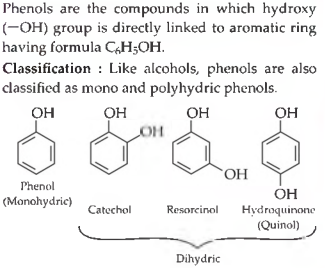
Primary	Secondary	Tertiary
RCH_2OH	$R^{R'}>CHOH$	$R^{R'}>C(R'')-OH$
P/I_2 or HI	P/I_2 or HI	P/I_2 or HI
RCH_2I	$R^{R'}>CHI$	$R^{R'}>C(R'')-I$
$AgNO_2$	$AgNO_2$	$AgNO_2$
RCH_2NO_2	$R^{R'}>CHNO_2$	$R^{R'}>C(R'')-NO_2$
HONO	HONO	HONO
$R-C(NOH)-NO_2$ Nitrolic acid	$R^{R'}>C(NO)-NO_2$ Pseudo nitrol	No reaction
NaOH	NaOH	NaOH
Blood red colour	Blue colour	Colourless

- **Lucas test** : Lucas reagent is a solution of conc. HCl with anhyd. $ZnCl_2$. With Lucas reagent,
  Primary alcohols – No cloudiness
  Secondary alcohols – Cloudiness in 5 minutes
  Tertiary alcohols – Cloudiness immediately
- **Catalytic dehydrogenation** :



PHENOLS

- Phenols are the compounds in which hydroxy (−OH) group is directly linked to aromatic ring having formula C_6H_5OH.
- **Classification** : Like alcohols, phenols are also classified as mono and polyhydric phenols.



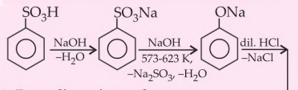
- **Nomenclature** : The simplest hydroxy derivative of benzene is phenol also called *carbolic acid*. It is its common name and also an accepted IUPAC name.
  - As structure of phenol involves a benzene ring, in its substituted compounds the terms *ortho*(1,2-disubstituted), *meta*(1,3-disubstituted) and *para*(1,4-disubstituted) are used in the common names.

Compound	Common name	IUPAC name
OH, CH3	*o*-Cresol	2-Methylphenol
OH, OH	Catechol	Benzene-1, 2-diol
OH, OH	Resorcinol	Benzene-1, 3-diol
OH, OH	Hydroquinone or quinol	Benzene-1, 4-diol
OH, OH, OH	Pyrogallol	Benzene-1, 2, 3-triol
OH, Br	*m*-Bromophenol	3-Bromophenol
OH, NH2	*o*-Aminophenol	2-Aminophenol
OH, NO2	*p*-Nitrophenol	4-Nitrophenol

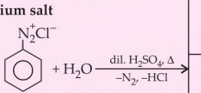
- **Structure :** In phenols, the — OH group is attached to sp^2 hybridised C atom of an aromatic ring.
  - The C — O bond length in phenol is slightly less than the C — O bond length in alcohol due to partial double bond character of C — O bond and sp^2 hybridised state of C atom to which O atom is attached.

Preparation

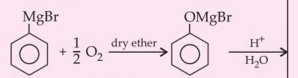
1. From benzenesulphonic acid



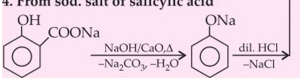
2. From diazonium salt



3. From phenylmagnesium bromide

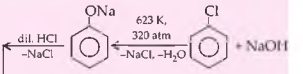


4. From sod. salt of salicylic acid

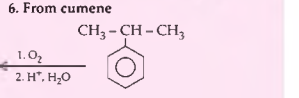


C_6H_5OH Phenol

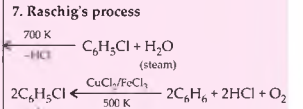
5. From haloarenes (Dow's process)



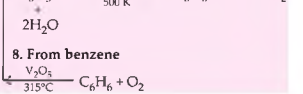
6. From cumene



7. Raschig's process



8. From benzene

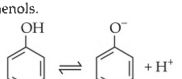


Physical Properties

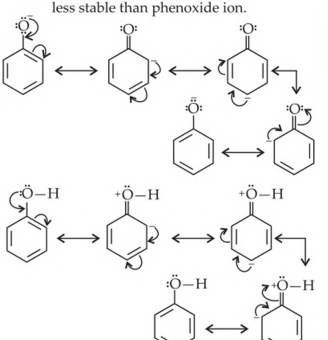
- **State and smell :** Phenols are colourless crystalline solids or liquids.
  - They have characteristic phenolic odours.
- **Boiling points :** Boiling points of phenols are much higher than the corresponding aromatic hydrocarbons and haloarenes due to involvement of intermolecular hydrogen bonding.
- **Solubility :** Like alcohols, phenols are soluble in water due to the formation of hydrogen bonding with water.
  - Phenols are less soluble than alcohols due to large hydrocarbon (benzene ring) part.

Chemical Properties

- **Acidic nature :** Phenols are more acidic than alcohols as the hydroxyl group in phenol is directly attached to highly electronegative sp^2 hybridised C atom of benzene ring which decreases the electron density on O atom.
  - Thus increases the polarity of O — H bond and results in an increase in ionisation of phenols.

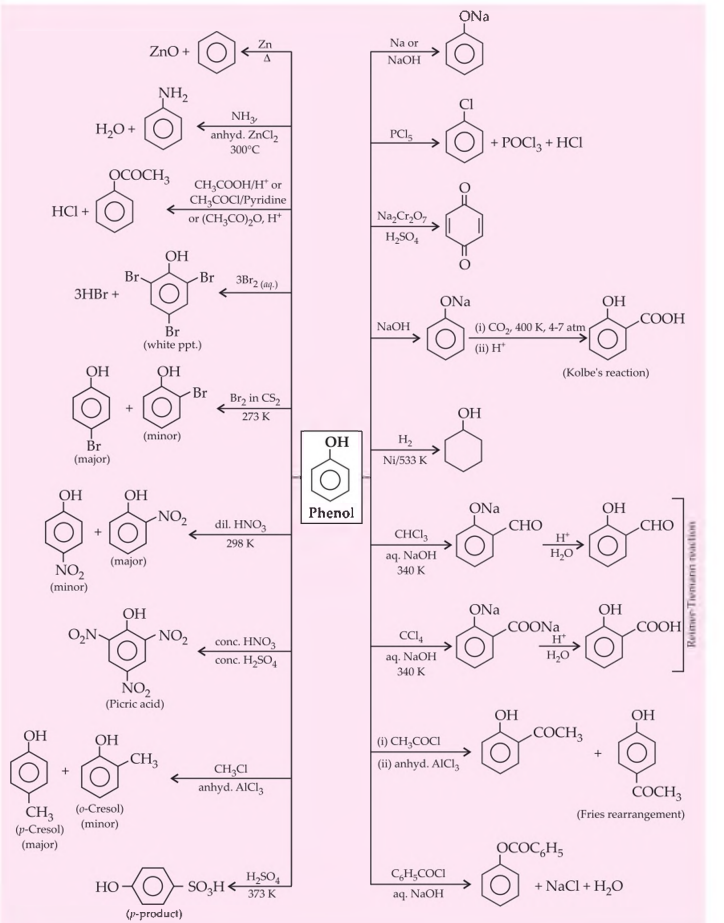


  - Moreover, in phenoxide ion, the charge is delocalised which makes phenoxide ion more stable thus favours the ionisation of phenol.
  - There is also charge delocalisation in phenol also, but its resonating structures have charge separation making phenol less stable than phenoxide ion.



  - An electron withdrawing group, increases the acidic strength of phenol in substituted phenol.
  - While an electron releasing group, decreases the acidic strength of phenol.

❑ Chemical Reactions

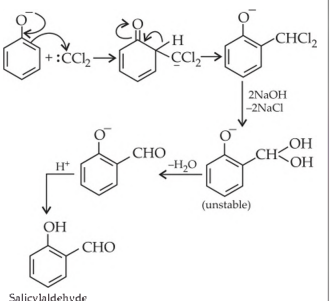


- **Mechanism of Riemer-Tiemann reaction**
  Reaction mechanism involves the electrophilic attack by dichlorocarbene generated from chloroform.

$$CHCl_3 + OH^- \rightleftharpoons :CCl_3^- + H_2O$$

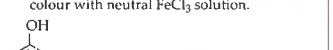
$$:CCl_3^- \longrightarrow :CCl_2 + Cl^-$$

Dichlorocarbene
(Attacking electrophile)

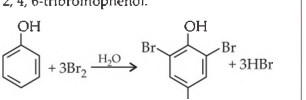


Salicylaldehyde

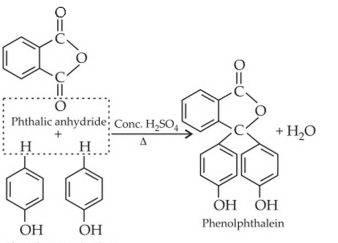
- **Test for Phenols**
  - **Ferric chloride test :** Phenol gives violet colour with neutral $FeCl_3$ solution.



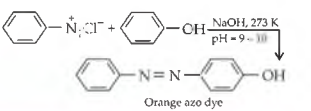
  - **Bromine water test :** Phenol gives white ppt. with Br_2-water due to the formation of 2, 4, 6-tribromophenol.



  - **Liebermann's nitroso test :** Phenol on reaction with $NaNO_2$ and conc. H_2SO_4 gives deep green or blue colour which changes into red on dilution with water.
  - **Phthalic anhydride test :** Phenol reacts with phthalic anhydride in presence of conc. H_2SO_4 and gives phenolphthalein which gives pink colour with alkali.



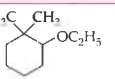
  - **Ammonia or sodium hypochlorite test :** Phenol gives blue colour.
  - **Coupling reaction :** Phenol gives orange azo dyes with diazonium salts in weakly basic solution.



Orange azo dye

ETHERS

- **General formula :** Ethers are the compounds having general formula $C_nH_{2n+2}O$ where n is always greater than 1.
- **Classification :** Ethers can be classified as symmetrical or simple ethers having formula $R-O-R$ and unsymmetrical or mixed ethers having formula $R-O-R'$.
- **Nomenclature :** Common names of ethers are derived from the names of alkyl/aryl groups written as separate words in alphabetical order and adding the word *'ether'* at the end.
  - If both the alkyl groups are the same, the prefix *'di'* is added before the alkyl group.
  - According to IUPAC system of nomenclature, ethers are regarded as hydrocarbon derivatives in which a hydrogen atom is replaced by an $-OR$ or $-OAr$ group, where R and Ar represent alkyl and aryl groups, respectively.
    - The larger R group is chosen as the parent hydrocarbon.

Compound	Common name	IUPAC name
$C_2H_5OC_2H_5$	Diethyl ether	Ethoxyethane
$CH_3OCH_2CH_2CH_3$	Methyl *n*-propyl ether	1-Methoxypropane
$C_6H_5OCH_2CH_3$	Ethyl phenyl ether (Phenetole)	Ethoxybenzene
$C_6H_5O(CH_2)_6CH_3$	Heptyl phenyl ether	1-Phenoxyheptane
$CH_3O-\underset{\displaystyle CH_3}{\overset{\displaystyle |}{CH}}-CH_3$	Methyl isopropyl ether	2-Methoxypropane
$CH_3O-CH_2-CH_2-OCH_3$	—	1,2-Dimethoxyethane
	—	2-Ethoxy-1,1-dimethylcyclohexane

- **Structure :** In ethers, the four electron pairs, *i.e.*, the two bond pairs and two lone pairs of electrons on O atom are arranged approximately in a tetrahedral arrangement.
  - The bond angle is slightly greater than the tetrahedral angle due to the repulsive interaction between the two bulky ($-R$) groups.
  - The C – O bond length (141 pm) is almost the same as in alcohols.

- **Preparation**

From alcohols by dehydration

$$2ROH \xrightarrow[\text{or } Al_2O_3,\ 523\ K]{\text{conc. } H_2SO_4,\ 413\ K} ROR$$

From alkyl halide

$$RX + RONa \xrightarrow[-NaX]{\Delta} ROR \quad \text{(Williamson synthesis)}$$

$$2RX + Ag_2O(dry) \xrightarrow[-AgX]{\Delta} ROR$$

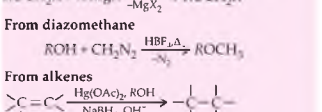
From Grignard reagent

$$ROCH_2X + R'MgX \xrightarrow[-MgX_2]{\text{Dry ether}} ROCH_2R'$$

From diazomethane

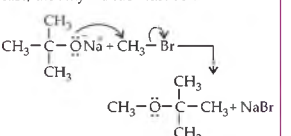
$$ROH + CH_2N_2 \xrightarrow[-N_2]{HBF_4,\Delta} ROCH_3$$

From alkenes

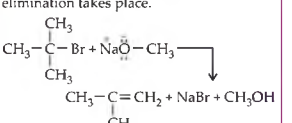


Key Points

- Williamson synthesis can be used to prepare ethers containing 2° or 3° alkyl groups through S_N2 mechanism. In this case, the alkyl halide must be 1°.



- In the case of 2° and 3° alkyl halides, elimination takes place.



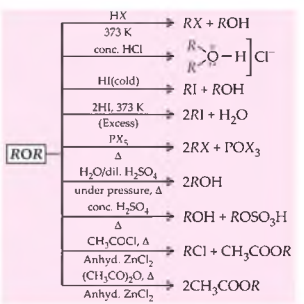
- Williamson synthesis method cannot be used to prepare diaryl ethers.
- Dehydration of alcohols for the formation of ethers follows the order :

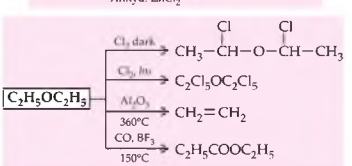
  1° > 2° > 3°

- **Physical Properties**
  - **Physical state :** Dimethyl ether and diethyl ether are exceptionally gases at room temperature while all other ethers are colourless liquids with characteristic etheral smell.

- **Polarity :** Due to bent structure, they have net dipole moment and therefore they are polar in nature.
- **Boiling points :** Boiling points of ethers are much lower than alcohols due to inability of forming hydrogen bonds.
- **Solubility :** Ethers are soluble in water to a certain extent due to hydrogen bonding.
  - However solubility decreases with increase of molecular mass.
  - Ethers are fairly soluble in all organic solvents such as alcohol, chloroform, benzene, etc.
- **Density :** Ethers are lighter than water.

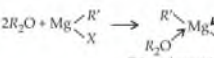
Chemical Reactions





Key Points

- **Reaction of ether with excess of HX:**
  - When one of the alkyl group is a 3° group, the halide formed is a 3° halide.
  - In case of anisole, the halide formed will be methyl iodide.
  - The order of reactivity with halogen acids follows: HI > HBr > HCl
- Ethers act as Lewis bases, form complexes with Lewis acids called etherates.



Grignard reagent etherate

ALDEHYDES AND KETONES

- **General formula :** These are the compounds with carbon-oxygen double bond (>C=O) called carbonyl group having general formula $C_nH_{2n}O$.
- **Aldehydes** contain carbonyl group attached to either two H atoms or one H atom and one C atom of an alkyl/aryl group.
- In **ketones**, the carbonyl group is attached to two C atoms of an alkyl/aryl group.
- **Nomenclature :** The common names of most aldehydes are derived from the common names of the corresponding carboxylic acids by replacing the ending *–ic'* of acid with aldehyde.
  - The location of the substituent in the carbon chain is indicated by Greek letters α, β, γ, δ, etc.
  - The common names of ketones are derived by naming two alkyl or aryl groups bonded to the carbonyl group.
  - The locations of substituents are indicated by Greek letters, α α', β β' and so on beginning with the carbon atoms next to the carbonyl group, indicated as α α'.
  - The IUPAC names of open chain aliphatic aldehydes and ketones are derived from the names of the corresponding alkanes by replacing the ending *–e'* with *–al'* and *–one'* respectively.

Compound	Common name	IUPAC name
$CH_3CH(OCH_3)CHO$	α-Methoxypropionaldehyde	2-Methoxypropanal
$CH_2=CHCHO$	Acrolein	Prop-2-enal
	m-Bromobenzaldehyde	3-Bromobenzenecarbaldehyde or 3-Bromobenzaldehyde
$(CH_3)_2CHCOCH(CH_3)_2$	Diisopropyl ketone	2,4-Dimethylpentan-3-one

- **Structure :** The C atom of carbonyl group is sp^2 hybridised and forms three σ bonds and one π bond with O atom.
  - Carbonyl carbon with three atoms attached to it lie in a same place with bond angle 120° and trigonal coplanar structure and π-electron cloud lies above and below of this plane.
- **Preparation**

Aldehydes and Ketones

1. Oxidation of alcohols

$$RCH_2OH + [O] \xrightarrow{K_2Cr_2O_7 + H_2SO_4} H_2O + RCHO$$

$$R_2CHOH + [O] \xrightarrow{K_2Cr_2O_7 + H_2SO_4} H_2O + R-\overset{\overset{O}{\|}}{C}-R$$

2. Oppenauer oxidation

$$R_2CHOH + (CH_3)_2CO \xrightarrow{Al[(CH_3)_3CO]_3} (CH_3)_2CHOH + RCOR$$

3. Catalytic dehydrogenation of alcohols

$$RCH_2OH \xrightarrow[573\ K]{Cu} RCHO + H_2\uparrow$$

$$R_2CHOH \xrightarrow[573\ K]{Cu} R_2CO + H_2\uparrow$$

4. Reductive ozonolysis of alkenes

$$RCH=CHR + O_3 \xrightarrow[196\ K]{CHCl_3 \text{ or } CCl_4} RCH\underset{O}{\overset{O}{\diagdown\diagup}}CHR \xrightarrow{Zn,\ H_2O} 2RCHO + ZnO$$

5. Rosenmund reduction

$$RCOCl + H_2 \xrightarrow[\text{boiling xylene}]{Pd\text{-}BaSO_4,\ S} RCHO + HCl$$

6. Reduction of nitriles

$$RC\equiv N \xrightarrow{\text{(i) } AlH(i\text{-}Bu)_2,\ \text{(ii) } H_2O} RCHO$$

$$RC\equiv N \xrightarrow{\text{(i) } R'MgX/\text{dry ether},\ \text{(ii) } H_3O^+} RCOR'$$

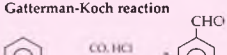
$$RC\equiv N \xrightarrow[\text{(ii) Ether, (iii) } H_2O]{\text{(i) } SnCl_2 + HCl} RCHO + NH_4Cl$$

(Stephen reduction)

7. From esters

$$RCOOR \xrightarrow[\text{(ii) } H_2O]{\text{(i) DIBAL-H, 195 K}} RCHO$$

8. Gatterman-Koch reaction



9. Friedel–Crafts acylation

10. From alkynes

$$-C\equiv C- \xrightarrow[H_2SO_4,\ 333\ K]{dil.\ H_2SO_4} RCHO \text{ or } RCOR$$

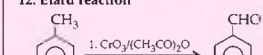
$$-C\equiv C- \xrightarrow[H_2O_2/OH^-]{B_2H_6,\ THF} RCHO \text{ or } RCOR$$

11. Oxidation of 1,2-glycols

$$R-\underset{OH}{CH}-\underset{OH}{CH}-R' + Pb(OOCCH_3)_4 \longrightarrow RCHO + R'CHO + 2CH_3COOH + (CH_3COO)_2Pb$$

$$\underset{R'}{\overset{R}{}}\!\!>\!\underset{OH}{C}-\underset{OH}{C}\!<\!\underset{R'}{\overset{R'}{}} \xrightarrow{[O]} RCOR + R'COR'$$

12. Etard reaction



13. Oxo process

$$RCH=CH_2 + CO + H_2 \xrightarrow[100°C,\ \text{pressure}]{[CoCO(H_2)_2} RCH_2CH_2CHO$$

14. Wacker process

$$H_2C=CH_2 + PdCl_2 + H_2O \xrightarrow[\text{Air or } O_2]{CuCl_2} CH_3CHO + Pd + 2HCl$$

15. From alkyl halides

$$RCH_2X + (CH_3)_2SO \longrightarrow RCHO + (CH_3)_2S + HX$$

$$R_2CHX + (CH_3)_2SO \longrightarrow R_2CO + (CH_3)_2S + HX$$

16. From lithium and cadmium salts

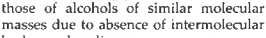
$$2RMgX + CdCl_2 \xrightarrow[\text{ether}]{\text{dry}} R_2Cd + MgCl_2 + MgX_2$$

$$R_2Cd + R'COCl \longrightarrow RCOR' + RCdCl$$

$$R-COO^-Li^+ + CH_3Li \longrightarrow R-\underset{OLi}{\overset{OH}{C}}-CH_3 \xrightarrow{H^+/H_2O} R-\underset{OH}{\overset{OH}{C}}-CH_3 \xrightarrow{-H_2O} R-\overset{\overset{O}{\|}}{C}-CH_3$$

Physical Properties

- **Physical state :** Lower members of aldehydes and ketones (upto C_{10}) are colourless volatile liquids except formaldehyde which is gas at ordinary temperature.
  - Higher members of aldehydes and ketones are solids with fruity odour.
  - Lower aldehydes have unpleasant odour but ketones possess pleasant smell.
- **Boiling points :** The boiling points of aldehydes and ketones are higher than hydrocarbons and ethers of comparable molecular masses.
  - It is due to weak molecular association in aldehydes and ketones arising out of the dipole-dipole interactions.
  - Also, their boiling points are lower than those of alcohols of similar molecular masses due to absence of intermolecular hydrogen bonding.

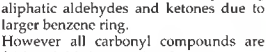


Intermolecular dipole-dipole interactions

Key Point

- Among isomeric aldehydes and ketones, ketones have slighty higher boiling points due to the presence of two electron releasing alkyl groups which make carbonyl group more polar.

- **Solubility :** Lower members of aldehydes and ketones (upto C_4) are soluble in water due to H-bonding between polar carbonyl group and water.
  - However, solubility decreases with increase in molecular weight.
  - Aromatic aldehydes and ketones are much less soluble than corresponding aliphatic aldehydes and ketones due to larger benzene ring.
  - However all carbonyl compounds are fairly soluble in organic solvents.



Chemical Properties

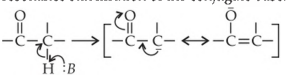
- **Polarity of carbonyl ($>C=O$) group :** Due to high electronegativity of O atom, the carbon-oxygen double bond is polar in nature having small positive charge on C atom and small negative charge on O atom and shows net dipole moment. Hence, the carbonyl carbon, is electrophilic in nature acts as Lewis acid and carbonyl oxygen, is nucleophilic in nature acts as Lewis base.

μ = 2.3 D $\quad$ μ = 2.8 D

Therefore aldehydes and ketones undergo nucleophilic addition reactions in contrast to alkenes which undergo electrophilic addition reactions.

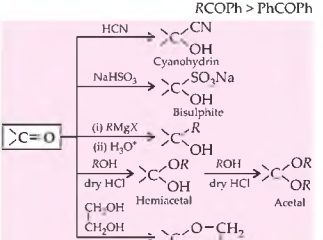
- **Acidity of α-hydrogen atoms**

The acidity of α-hydrogen atoms of carbonyl compounds is due to the strong electron withdrawing effect of the carbonyl group and resonance stabilisation of the conjugate base.

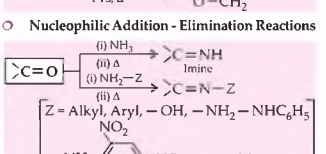


- **Nucleophilic Addition Reactions**
  - **Relative reactivities of aldehydes and ketones:** Aldehydes are generally more reactive than ketones in nucleophilic addition reactions due to steric and electronic reasons.
  - Sterically, the presence of two relatively large substituents in ketones hinders the approach of nucleophile to carbonyl carbon than in aldehydes having only one such substituent.
  - Electronically, aldehydes are more reactive than ketones because two alkyl groups reduce the electrophilicity of the carbonyl more effectively than in former.

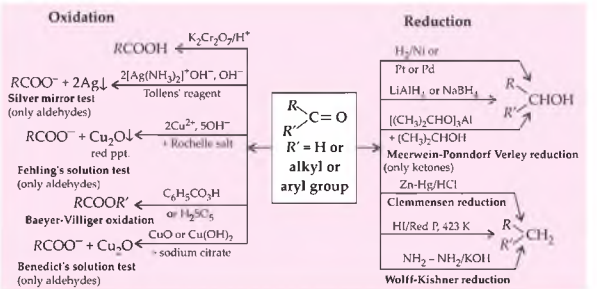
HCHO > RCHO > PhCHO > RCOR > RCOPh > PhCOPh



- **Nucleophilic Addition - Elimination Reactions**



Oxidation and reduction reactions



Haloform reaction

Given by methyl ketones (even acetaldehyde).

$2NaOH + I_2 \longrightarrow NaI + NaOI + H_2O$

$RCOCH_3 + 3NaOI \longrightarrow RCOONa + \underset{\text{Iodoform (yellow ppt.)}}{CHI_3\downarrow} + 2NaOH$

Reactions involving α-hydrogen atom

- **Aldol condensation:** Aldehydes and ketones having at least one α-hydrogen undergo a reaction in the presence of dilute alkali as catalyst to form β-hydroxy aldehydes (aldol) or β-hydroxy ketones (ketol), respectively.
- The aldol and ketol readily lose water to give α, β-unsaturated carbonyl compounds.

$$2R-\overset{\alpha}{CH_2}-\overset{O}{\overset{\|}{C}}-H \xrightarrow{\text{dil. NaOH}} \underset{\text{Aldol}}{R-CH_2-\underset{OH}{\underset{|}{CH}}-\underset{R}{\underset{|}{CH}}-\overset{O}{\overset{\|}{C}}-H} \xrightarrow[-H_2O]{\Delta} \underset{\alpha,\beta\text{-Unsaturated aldehyde}}{R-CH_2-CH=\underset{R}{\underset{|}{C}}-\overset{O}{\overset{\|}{C}}-H}$$

- **Intramolecular aldol condensation:** It takes place in diketones and gives rise to cyclic products.
- **Crossed aldol condensation:** Aldol condensation is carried out between two different aldehydes and/or ketones.
  - If both of them contain α-hydrogen atoms, it gives a mixture of four products.

CH_3CHO + CH_3CH_2CHO

1. NaOH, 2. Δ

- $CH_3-CH=CH-CHO$
- $CH_3CH_2-CH=\underset{CH_3}{\underset{|}{C}}-CHO$

(Self aldol products)

- $CH_3-CH=\underset{CH_3}{\underset{|}{C}}-CHO$
- $CH_3CH_2-CH=CH-CHO$

(Cross aldol products)

Reactions involving no α-hydrogen atom

- **Cannizzaro reaction:** Only those aldehydes which do not have an α-hydrogen atom undergo self-oxidation and reduction reaction on treatment with concentrated alkali. In this reaction, one molecule of aldehyde is reduced to alcohol while another is oxidised to carboxylic acid salt.

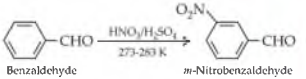
$$\underset{\text{Formaldehyde}}{HCHO} + HCHO \xrightarrow{\text{conc. KOH}} \underset{\text{Methanol}}{CH_3OH} + \underset{\text{Potassium formate}}{HCOOK}$$

- **Crossed Cannizzaro reaction:**

$$C_6H_5-\overset{O}{\overset{\|}{C}}-H + H-\overset{O}{\overset{\|}{C}}-H \xrightarrow[\Delta]{OH^-} \underset{\text{Benzyl alcohol}}{C_6H_5CH_2OH} + \underset{\text{Sod. formate}}{HCOONa}$$

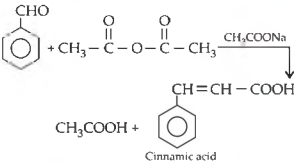
- **Intramolecular Cannizzaro reaction:** It is given by dialdehydes having no α-hydrogen atoms.

- **Electrophilic Substitution Reaction**
  - Aromatic aldehydes and ketones undergo electrophilic substitution at the ring in which the carbonyl group acts as a deactivating and *meta* directing group.



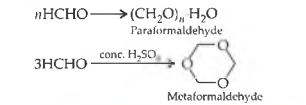
Benzaldehyde — *m*-Nitrobenzaldehyde

  - **Perkin reaction**



Cinnamic acid

  - **Polymerisation**



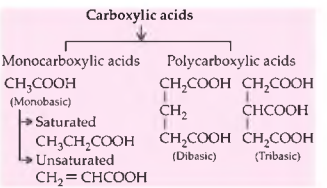
Metaformaldehyde

- **Distinction between aldehydes and ketones**

Tests with	Aldehydes	Ketones
Schiff's reagent	Pink colour	No colour
Fehling's solution	Red precipitate	No precipitate
Tollens' reagent	Black precipitate of silver or silver mirror	No black ppt. or silver mirror
2,4-Dinitro-phenyl-hydrazine	Orange-yellow or red well defined crystals with melting points characteristic of individual aldehydes.	Orange-yellow or red well defined crystals with melting points characteristic of individual ketones.
Sodium hydroxide	Give brown resinous mass (formaldehyde does not give this test).	No reaction
Alkaline sodium nitroprusside	A deep red colour (formaldehyde does not respond to this test).	Red colour which changes to orange.

CARBOXYLIC ACIDS

- **General formula** : Compounds having —COOH group having general formula $C_nH_{2n}O_2$.
- **Classification** : Like alcohols, carboxylic acids are also classified as monocarboxylic acids and polycarboxylic acids depending upon number of carboxyl groups present in a molecule.

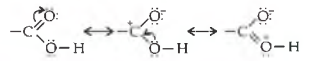


- **Nomenclature** : The common names end with the suffix *–'ic acid'* and have been derived from Latin or Greek names of their natural sources. For example, formic acid (HCOOH) was first obtained from red ants (Latin: *formica* means ant), acetic acid (CH_3COOH) from vinegar (Latin: *acetum*, means vinegar).
  - In the IUPAC system, aliphatic carboxylic acids are named by replacing the ending *–'e'* in the name of the corresponding alkane with *–'oic acid'*. In numbering the carbon chain, the carboxylic carbon is numbered one.

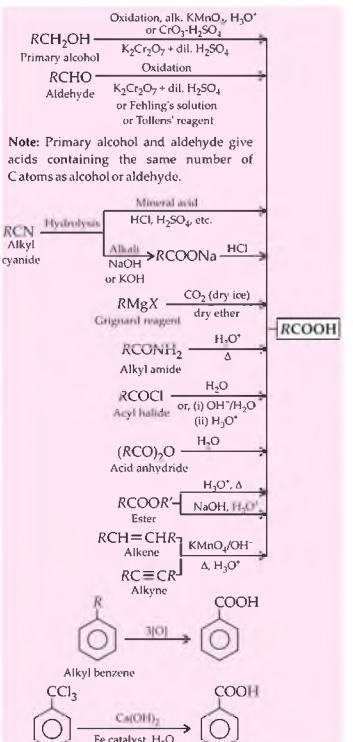
Compound	Common name	IUPAC name
CH_3COOH	Acetic acid	Ethanoic acid
$(CH_3)_2CHCOOH$	Isobutyric acid	2-Methylpropanoic acid
$HOOC-COOH$	Oxalic acid	Ethanedioic acid
$HOOC-(CH_2)_2-COOH$	Succinic acid	Butanedioic acid
	Phenylacetic acid	2-Phenylethanoic acid

❑ **Structure :** In carboxylic acids, the bonds to the carboxyl carbon lie in one plane and are separated by about 120°.

- The carboxylic carbon is less electrophilic than carbonyl carbon because of the possible resonance structure.

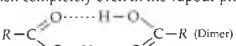


❑ **Preparation**



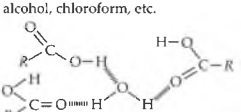
❑ **Physical Properties**

- **Physical state :** The lower fatty acids upto C_9 are colourless liquids. The higher ones are colourless waxy solids.
- **Odour :** The first three members have a sharp pungent odour. The middle ones, C_4 to C_9, have an odour of rancid butter. The higher members do not possess any smell.
- **Boiling points :** Carboxylic acids are higher boiling liquids than aldehydes, ketones and even alcohols of comparable molecular masses due to more extensive association of their molecules through intermolecular hydrogen bonding. The H-bonds are not broken completely even in the vapour phase.



(in vapour state or in aprotic solvent)

- **Solubility :** Simple aliphatic carboxylic acids having upto four carbon atoms are miscible in water due to the formation of hydrogen bonds with water.
  - The solubility decreases with increasing number of carbon atoms. Higher carboxylic acids are practically insoluble in water due to the increased hydrophobic interaction of hydrocarbon part.
  - Benzoic acid, the simplest aromatic carboxylic acid is nearly insoluble in cold water.
  - Carboxylic acids are also soluble in less polar organic solvents like benzene, ether, alcohol, chloroform, etc.

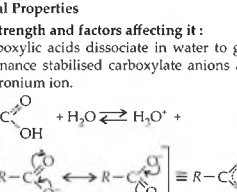


(Hydrogen bonding of RCOOH with H_2O)

❑ **Chemical Properties**

Acidic strength and factors affecting it :

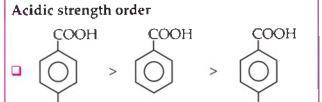
- Carboxylic acids dissociate in water to give resonance stabilised carboxylate anions and hydronium ion.



- Carboxylic acids are weaker acids than mineral acids, but they are stronger acids than alcohols and many simple phenols.
- The conjugate base of carboxylic acid, a carboxylate ion, is stabilised by two equivalent resonance structures. The negative charge in these structures is delocalised over two more electronegative oxygen atoms. The conjugate base of phenol, a phenoxide ion, has non-equivalent resonance structures in which the negative charge is at the less electronegative carbon atom.
- Electron withdrawing group stabilises the carboxylate anion and strengthens the acid through delocalisation of the negative charge through inductive effect. More the number of electron withdrawing groups, more will be the acidic strength.
- More is the distance between the carboxyl group and electron withdrawing group, lesser will be the acidic strength.
  $FCH_2CH_2COOH < FCH_2COOH < CF_3COOH$
- Acidic strength decreases as the $+I$ effect of the alkyl group increases.
  $(CH_3)_3CCOOH < (CH_3)_2CHCOOH < CH_3COOH < HCOOH$
- $-CH_3$ group being electron releasing, decreases the acidity while as formic acid does not contain alkyl group, it is stronger acid. Phenyl group increases the acidity contrary to the decrease expected due to resonance effect.
  $HCOOH > C_6H_5COOH > CH_3COOH$
- More the electronegativity of the atom attached to the carboxyl group (F > Cl > H), more will be the acidity.
  $FCOOH > ClCOOH > HCOOH$

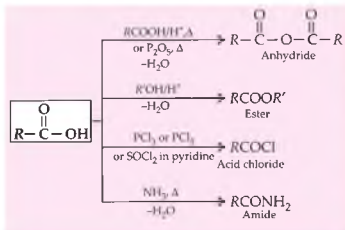
Key Points

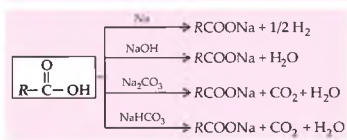
Acidic strength order



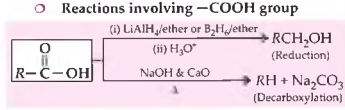
- $C_6H_5COOH > CH_3COOH > C_6H_5OH$
- $CF_3COOH > CCl_3COOH > CHCl_2COOH > NO_2CH_2COOH > NCCH_2COOH > FCH_2COOH > ClCH_2COOH > BrCH_2COOH > HCOOH > ClCH_2CH_2COOH > C_6H_5COOH > C_6H_5CH_2COOH > CH_3COOH > CH_3CH_2COOH$

- **Chemical Reactions**
  - **Reactions involving cleavage of C – OH bond**





  - **Reactions involving –COOH group**

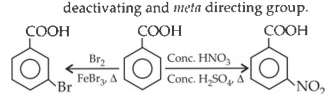


  - **Hell-Volhard Zelinsky reaction**

$$RCH_2COOH \xrightarrow[\text{(ii) } H_2O]{\text{(i) } X_2/R\text{-}red\ P} R-\underset{\underset{X}{|}}{CH}-COOH$$

α-Halocarboxylic acid

  - **Ring substitution in aromatic acids**
    - Aromatic carboxylic acids undergo electrophilic substitution reactions in which the carboxyl group acts as a deactivating and *meta* directing group.



- **Ester hydrolysis**

$$R-\overset{O}{\overset{\|}{C}}-OR' + H_2O \underset{\text{or } OH^-}{\overset{H^+}{\rightleftharpoons}} R-\overset{O}{\overset{\|}{C}}-OH + R'OH$$

- **Distinction test between Phenol and Carboxylic acid**

Test	Phenol	Carboxylic acid
$NaHCO_3$ test	No reaction	Brisk effervescence of CO_2 gas.
$FeCl_3$ test	Violet colour	Buff coloured ppt.

- **Uses**
  - **Methanol** is used as a solvent for paints, varnishes and celluloid, etc. and as an antifreeze for automobile radiators.
  - **Ethanol** is used as an antiseptic in form of rectified spirit, important beverage, *i.e.*, beer, rum, whisky, brandy, etc.
  - **Phenol** is used as an antiseptic and disinfectant in soaps and lotions, in the manufacture of drugs like aspirin, salol, salicylic acid, phenacetin, etc. and in the manufacture of azo dyes.
  - **Formaldehyde** is used for the preservation of biological specimens and in the manufacture of bakelite, urea-formaldehyde glues.
  - **Benzaldehyde** is used as a flavouring agent in perfume industry and in the manufacture of dyes like malachite green.
  - **Acetone** is used as solvent in industry and as nail polish remover.
  - **Carboxylic acids**
    - Ethanoic acid is widely used as a solvent and as vinegar in food industry. It is also used in the manufacture of plastics, rayon and silk.
    - Sodium benzoate is used as a preservative for tomato sauce (ketchup), fruit jams and juices in food industry.
    - Higher fatty acids are used for the manufacture of soaps and detergents.

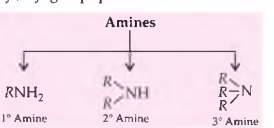
ORGANIC COMPOUNDS CONTAINING NITROGEN

- Introduction
- Classification, Nomenclature, Structure, Preparation, Properties, Distinction
- Amines
- Aniline
- Diazonium salts

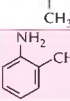
TIPS TO REMEMBER

AMINES

- Amines are the ammonia derivatives obtained by replacing one, two or three hydogen atoms by alkyl/aryl groups.
- **Classification :** Amines can be classified as 1°, 2° or 3° amines depending on the number of alkyl/aryl groups present in ammonia molecule.

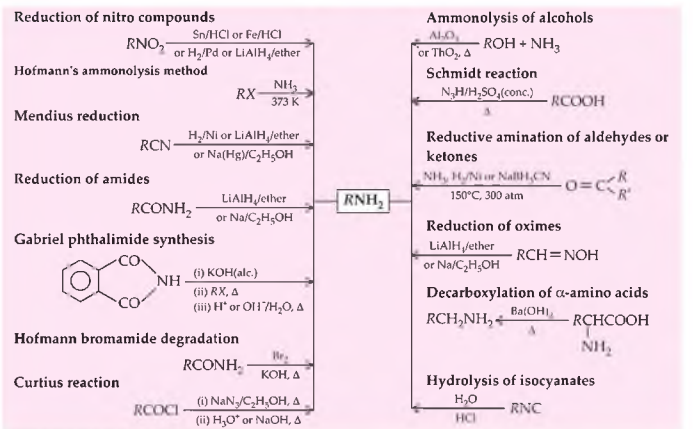


- **Nomenclature :** In common system, an aliphatic amine is named by prefixing alkyl group to amine, *i.e.*, alkylamine as one word.
  - In secondary and tertiary amines, when two or more groups are the same, the prefix *di* or *tri* is appended before the name of alkyl group.
  - In IUPAC system, amines are named as *alkanamines*, derived by replacement of '*e*' of alkane by the word '*amine*'.

Compound	Common name	IUPAC name
$CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\underset{\displaystyle |}{N}}}-CH_3$	Trimethylamine	*N,N*-Dimethylmethanamine
	*o*-Toluidine	2-Aminotoluene
	N,N-Dimethylaniline	*N,N*-Dimethylbenzenamine

- **Structure :** Nitrogen atom of amines is trivalent and carries an unshared pair of electrons. Nitrogen orbitals in amines are therefore, sp^3 hybridised and the geometry of amines is pyramidal. Due to the presence of unshared pair of electrons, the angle C – N – *R*, (where *R* is C or H) is less than 109.5°.

- **Preparation**



Key Points

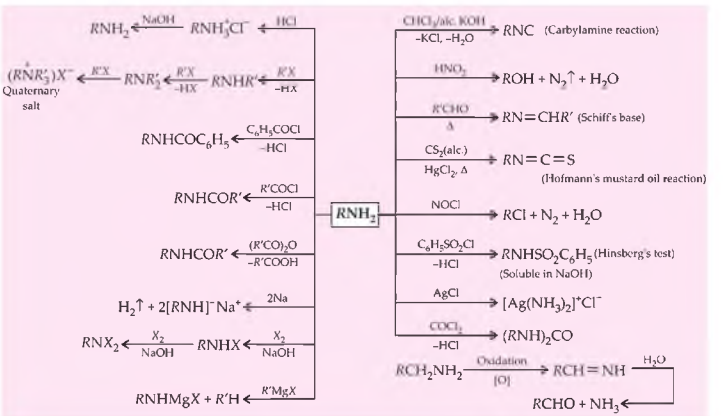
- Gabriel phthalimide synthesis is used for the preparation of 1° amines.
- Aromatic 1° amines cannot be prepared by this method because aryl halides do not undergo nucleophilic substitution reaction with potassium phthalimide under mild conditions.
- *tert*-Butylamine is a 1° amine, but cannot be prepared by this method. In this case, elimination takes place.

- **Physical Properties**
  - **Physical state :** Lower aliphatic amines are gases with smell like ammonia.
    - Primary amines with C_3 or more are liquids with fishy odour.
    - Lower aromatic amines are liquids with characteristic unpleasant odour but higher ones are solids which are odourless.
  - **Colour :** Pure amines are colourless but get coloured due to atmospheric oxidation.
  - **Solubility :** Amines are soluble in water as they can form hydrogen bonds with water.
    - As the size of alkyl group increases, solubility decreases.
    - Higher amines are insoluble in water but soluble in organic solvents.
    - Aromatic amines are insoluble in water. They are soluble in organic solvents such as benzene, ether, alcohol.
  - **Boiling points :** Amines being polar, form intermolecular hydrogen bonds and exist as associated molecules, therefore, shows higher boiling points than hydrocarbons of comparable molecular masses.
    - Tertiary amines have the lowest boiling point as they do not have hydrogen atoms linked to the nitrogen atom.
    - The intermolecular association is more in primary amines than in secondary amines due to presence of two hydrogen atoms. Therefore, the order of boiling points of isomeric amines is 1° > 2° > 3°.

Chemical Properties : Basic character of amines

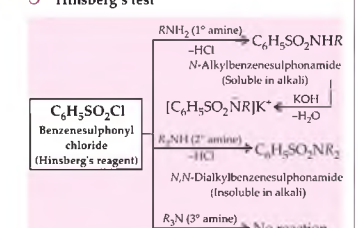
- Amines are basic in nature, due to the presence of lone pair of electrons on nitrogen atom.
- Aliphatic amines are stronger bases than ammonia due to the *+I* effect of alkyl groups present in amines.
- Aromatic amines are weaker bases than ammonia due to *–I* effect of aryl group.
- Besides inductive effect, there are other effects like steric effect, solvation effect, resonance effect which effect the basic strength of amines.
- In gaseous phase, the order of basicity of amines is
  3° amine > 2° amine > 1° amine > NH_3.
- In aqueous phase, despite of inductive effect, solvation effect and steric hindrance also play an important role. Thus, the order of basicity of amines is
  - $(C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_2 > NH_3$
  - $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$

Chemical Reactions

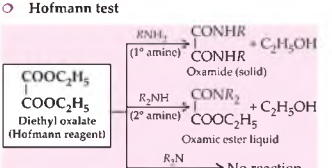


Distinction between 1°, 2° and 3° amines

Hinsberg's test



Hofmann test



- **Carbylamine test :** Only aliphatic and aromatic primary amines give this test.
  - Secondary and tertiary amines will not give this test.

CONCEPT MAP — EQUILIBRIUM

Chemical Equilibrium

- Involves chemical changes
  $A + B \rightleftharpoons C + D$
  Rate of forward reaction = Rate of reverse reaction
- Also called dynamic equilibrium

Law of Chemical Equilibrium

- $xA_{(aq)} + yB_{(aq)} \rightleftharpoons mC_{(aq)} + nD_{(aq)}$

$$K_c = \frac{[C]^m [D]^n}{[A]^x [B]^y}$$

- $xA_{(g)} + yB_{(g)} \rightleftharpoons mC_{(g)} + nD_{(g)}$

$$K_p = \frac{(p_C)^m (p_D)^n}{(p_A)^x (p_B)^y}$$

Relation between K_p and K_c

- $K_p = K_c(RT)^{\Delta n}$
  - If $\Delta n = 0$, $K_p = K_c$
  - If Δn = +ve, $K_p > K_c$
  - If Δn = −ve, $K_p < K_c$
- Equilibrium constant for the reverse reaction (K_c')

$$K_c' = \frac{1}{K_c}$$

- Equilibrium constant for the reaction which is divisible by n

$$K_c' = \sqrt[n]{K_c}$$

- Equilibrium constant for the reaction which is multiplied by n

$$K_c' = (K_c)^n$$

- Equilibrium constant for the reaction taking place in n steps

$$K_c' = K_1 \times K_2 \times K_3 \ldots K_n$$

Types of Chemical Equilibrium

- **Homogeneous Equilibrium :** All the reactants and products are in the same phase.
  $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$
- **Heterogeneous Equilibrium :** Reactants and products are in two or more different phases.
  $C_{(s)} + H_2O_{(g)} \rightleftharpoons CO_{(g)} + H_{2(g)}$

Physical Equilibrium

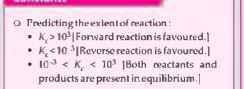
Involves physical changes

Phase Transformation Processes

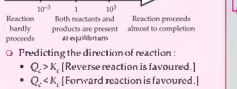
- **Solid-Liquid Equilibrium :** $r_{\text{Melting of ice}} = r_{\text{Freezing of water}}$
- **Liquid-Gas Equilibrium :** $r_{\text{Evaporation}} = r_{\text{Condensation}}$
- **Solid-Gas Equilibrium :** $r_{\text{Sublimation}} = r_{\text{Condensation}}$
- **Solid-Solution Equilibrium :** $r_{\text{Dissolution}} = r_{\text{Crystallisation}}$
- **Gas-Solution Equilibrium :** $m \propto p$ [Henry's law]

Applications of Equilibrium Constants

- Predicting the extent of reaction :
  - $K_c > 10^3$ [Forward reaction is favoured.]
  - $K_c < 10^{-3}$ [Reverse reaction is favoured.]
  - $10^{-3} < K_c < 10^3$ [Both reactants and products are present in equilibrium.]



- Predicting the direction of reaction :
  - $Q_c > K_c$ [Reverse reaction is favoured.]
  - $Q_c < K_c$ [Forward reaction is favoured.]
  - $Q_c = K_c$ [Reaction is in equilibrium.]



Relation between Gibbs Free Energy and Equilibrium Constant

- At equilibrium
  $\Delta G^\circ = -RT \ln K$; $K = e^{-\Delta G^\circ/RT}$
  - If $\Delta G^\circ < 0$ then $K > 1$ [Forward reaction is favoured.]
  - If $\Delta G^\circ > 0$ then $K < 1$ [Reversed reaction is favoured.]
  - If $\Delta G^\circ = 0$, then $K = 1$ [Reaction is in equilibrium.]

Factors Affecting Equilibrium

Le-Chatelier's principle

- **Change in Concentration:** If concentration of any reactant or product is increased, the equilibrium will shift in a direction where it is being consumed.
- **Change in Temperature:** If temperature is increased, reaction will proceed in the direction where heat is absorbed.
- **Change in Pressure :** If pressure is increased, then equilibrium will shift in a direction where number of moles reduces.
- **Addition of Inert Gas:**
  - **At Constant Volume :** No change in equilibrium
  - **At Constant Pressure:** Equilibrium will shift towards greater number of moles.
- **Catalyst :** No change in equilibrium. It helps in attaining the equilibrium quickly.

Ionic Equilibrium

Involves ionisation processes

Ionisation

- **Ionisation of Acids:**
  $HA_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + A^-_{(aq)}$

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

K_a = ionisation constant,
$pK_a = -\log K_a$
As K_a increases, pK_a decreases and acidity increases.

- **Ionisation of Bases :**
  $BOH_{(aq)} \rightleftharpoons B^+_{(aq)} + OH^-_{(aq)}$

$$K_b = \frac{[B^+][OH^-]}{[BOH]} = \frac{C\alpha^2}{1-\alpha}$$

$pK_b = -\log K_b$
As K_b increases, pK_b decreases and basicity increases.

Ionic Product of Water

$2H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)}$

K_w = $[H_3O^+][OH^-] = 1 \times 10^{-14}\ M^2$
$\therefore [OH^-] = [H^+] = 1.0 \times 10^{-7}$ M at 298 K

pH

- $pH = -\log[H_3O^+] = -\log[10^{-7}] = 7$

Solution	$[H^+]$	$[OH^-]$	pH	pOH
Acidic	$>10^{-7}$	$<10^{-7}$	<7	>7
Basic	$<10^{-7}$	$>10^{-7}$	>7	<7
Neutral	10^{-7}	10^{-7}	7	7

- $pK_w = pH + pOH = 14$

Buffer Solution

It is a solution which resists change in pH on dilution or with the addition of small amounts of acid or alkali.

- **Acidic Buffer :** Mixture of weak acid + salt of this weak acid with strong base. *e.g.* $CH_3COOH + CH_3COONa$

$$pH = pK_a + \log \frac{[Salt]}{[Acid]}$$

- **Basic Buffer :** Mixture of weak base and salt of this weak base with strong acid. *e.g.* $NH_4OH + NH_4Cl$

$$pOH = pK_b + \log \frac{[Salt]}{[Base]}$$

Solubility Product

- $A_{xy}B_{y(s)} \rightleftharpoons mA^{n+} + nB^{m-}$
  $K_{sp} = [A^{n+}]^m [B^{m-}]^n$
  - $K_{ip} > K_{sp}$, Precipitation occurs.
  - $K_{ip} < K_{sp}$, Precipitation does not occur.
  - $K_{ip} = K_{sp}$, Solution is saturated.

Relation between Solubility and Solubility Product

$$\left.\begin{aligned} K_{sp} &= [mS]^m [nS]^n \\ &= m^m S^m \cdot n^n S^n \\ &= m^m \cdot n^n \cdot (S)^{m+n} \end{aligned}\right\} \text{[where } S \text{ is solubility.]}$$

Hydrolysis of Salts

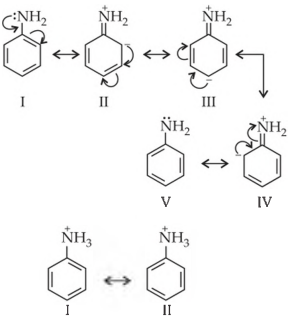
It is a process in which a salt reacts with water to give acid and base.

- **Salt of Strong Base and Strong Acid :** Neutral solution, *e.g.*, NaCl, KCl
- **Salt of Weak Base and Strong Acid :**
  $K_h = \frac{K_w}{K_b}$; $pH = \frac{1}{2}[pK_w - pK_b - \log C]$
  e.g., NH_4Cl, $CuSO_4$
- **Salt of Strong Base and Weak Acid :**
  $K_h = \frac{K_w}{K_a}$; $pH = \frac{1}{2}[pK_w + pK_a + \log C]$
  e.g., CH_3COONa, Na_3PO_4
- **Salt of Weak Acid and Weak Base:**
  $K_h = \frac{K_w}{K_a \times K_b}$; $pH = \frac{1}{2}[pK_w + pK_a - pK_b]$
  e.g., CH_3COONH_4, $AlPO_4$

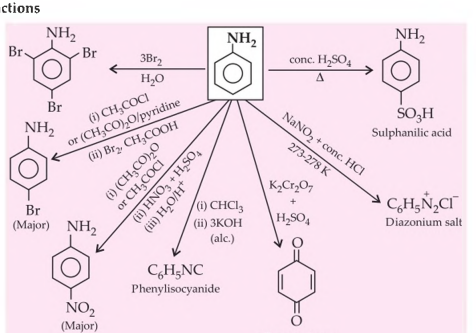
- **Azo dye test :** Only primary aromatic amines will give orange coloured azo dyes.
- **Hofmann mustard oil reaction :** Both aromatic and aliphatic primary amines give this test.
  - Aliphatic primary amines on heating with CS_2 and $HgCl_2$ give characteristic smell like mustard oil.
  - Aromatic primary amines on heating with ethanolic CS_2 and solid KOH give *N,N'*-diphenylthiorea which on treatment with conc. HCl gives phenyl isothiocyanate.
- **Nitrous acid test :** Aromatic primary amines react with nitrous acid at 0-5°C and gives benzenediazonium salts.
  - Aliphatic primary amines react with cold nitrous acid at 0-5°C and gives alcohols with the evolution of nitrogen gas.
  - Both secondary aliphatic and aromatic amines with nitrous acid give yellow oily compounds called *N*-nitrosamines.
  - Tertiary aliphatic amines with nitrous acid give water soluble nitrite salts.

ANILINE

- It is an aromatic amino compound in which the nitrogen atom of amino group is directly attached to aromatic ring.
- **Basic character of aromatic amines**
  - Aniline is less basic than alkylamines, due to the resonance of lone pair of electrons of nitrogen atom with benzene ring.
  - Moreover the anilinium ion obtained by accepting a proton have only two resonating structures.



  - Electron withdrawing groups decrease whereas electron donating groups increase the basic strength in case of substituted aniline.
- **Chemical Properties**
  - Aniline undergoes electrophilic substitution reactions. $-NH_2$ group is *ortho* and *para* directing groups.
- **Chemical Reactions**



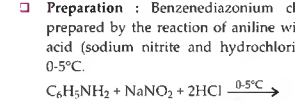
DIAZONIUM SALTS

- Arenediazonium salts have the general formula $ArN_2^+X^-$, Ar stands for the aryl ($-C_6H_5$) group and X^- is Cl^-, Br^-, NO_3^-, HSO_4^-, BF_4^-.
- **Nomenclature :** They are named by suffixing diazonium to the name of parent hydrocarbon followed by anion.
- **Preparation :** Benzenediazonium chloride is prepared by the reaction of aniline with nitrous acid (sodium nitrite and hydrochloric acid) at 0-5°C.

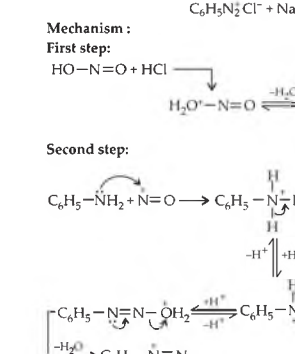
$$C_6H_5NH_2 + NaNO_2 + 2HCl \xrightarrow{0\text{-}5°C} C_6H_5N_2^+Cl^- + NaCl + 2H_2O$$

Mechanism :

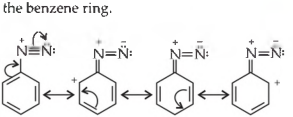
First step:



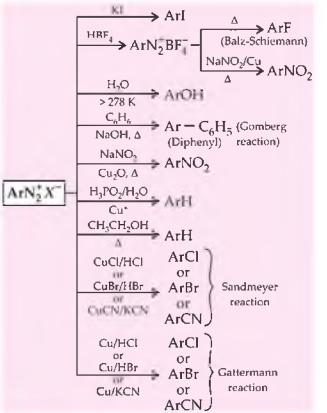
Second step:



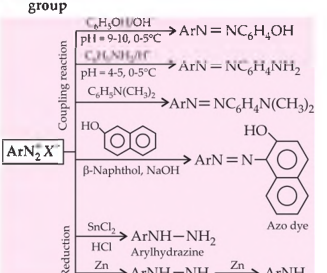
- **Stability :** Arenediazonium salts are more stable (for short time) than alkanediazonium salts due to dispersal of positive charge over the benzene ring.



- **Physical Properties:** These are generally colourless, crystalline solids, which are soluble in water.
  - They are unstable and explode in dry state.
- **Chemical Properties**
  - **Reactions involving displacement of diazo group**



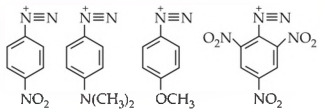
- **Reactions involving retention of diazo group**



- **Uses**
  - Diethylamine, triethylamine, etc. are used as reagents in organic synthesis and as solvents in the laboratory and industry.
  - Quaternary ammonium salts derived from long chain aliphatic tetriary amines are used as detergents.
  - Aromatic amines such as aniline are widely used in the manufacture of dyes and drugs.
  - Diazonium salts have many synthetic applications for preparing those substituted aromatic compounds which cannot be prepared by direct substitution in benzene.

Questions for Practice

1. The correct order of reactivity of the following ions towards azo coupling reactions under similar conditions is



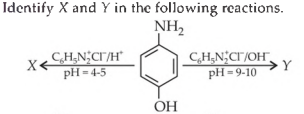
I II III IV

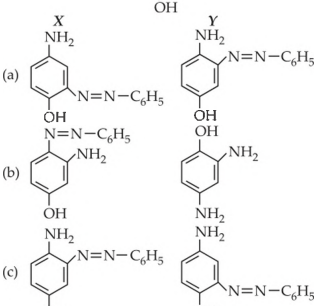
(a) I < II < III < IV (b) II > I > IV > III
(c) II < III < I < IV (d) III > IV > I > II

2. Which of the following is the weakest base in aqueous solution?
(a) Aniline (b) Trimethylamine
(c) Methylamine (d) Ammonia

3. The major product formed in reaction of 3-methylbutan-2-ol with conc. HCl is
(a) 2-chloro-2-methylbutane
(b) 2-chloro-3-methylbutane
(c) 2-methylbut-2-ene (d) 2-methylbut-1-ene

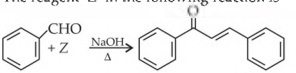
4. Identify *X* and *Y* in the following reactions.

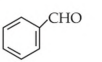
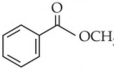
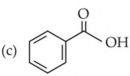
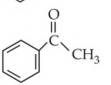




(d) Both *X* and *Y* are

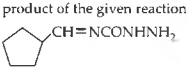
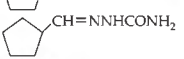
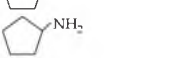
5. The reagent 'Z' in the following reaction is



(a) 
(b) 
(c) 
(d) 

6.

The product of the given reaction is

(a) 
(b) 
(c) 
(d) Both (a) and (b)

7. What product will be formed in the given reaction?

(a) $(CH_3)_2C=O$ (b) $(CH_3)_2\underset{OH}{C}-\underset{OH}{C}(CH_3)_2$
(c) $(CH_3)_2CHCOOH$ (d) $(CH_3)_2CHCHO$

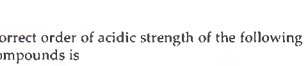
8. Acetone on condensation with chloroform in the presence of alkali gives a product which is used as hypnotic. Identify the product.
(a) Urotropine (b) Chloretone
(c) Paraformaldehyde (d) Benzoin

9. Phenol with carbon tetrachloride in presence of aqueous potassium hydroxide at 340 K followed by hydrolysis gives
(a) acetylsalicylic acid (b) salicylaldehyde
(c) salicylic acid (d) methyl salicylate

10. Cumene $\xrightarrow[\text{(ii) } H_2O/H^+]{\text{(i) } O_2} P + Q$

Identify *P* and *Q*.
(a) Propene, Phenol (b) Phenol, Toluene
(c) Acetaldehyde, Phenol
(d) Phenol, Acetone

11. Correct order of acidic strength of the following compounds is



(a) I > II > III > IV (b) III > II > I > IV
(c) IV > II > III > I (d) II > III > IV > I

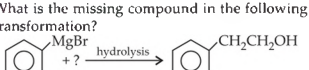
12. Which of the following amides will not undergo Hofmann bromamide degradation reaction?
(a) CH_3CONH_2 (b) $CH_3CH_2CONH_2$
(c) $C_6H_5CONH_2$ (d) $CH_3CONHCH_3$

13. The Hinsberg's test of a compound, $C_5H_{14}N_2$ produces a solid that is insoluble in 10% aq. NaOH. This solid derivative dissolves in 10% aqueous sulphuric acid. Which of the following would best describe these facts?
(a) $NH_2CH_2CH_2N(CH_3)_2$
(b) $(CH_3)_2NCH_2CH_2NHCH_3$
(c) $NH_2CH_2C(CH_3)_2CH_2NH_2$
(d) $(CH_3)_2NCH_2N(CH_3)_2$

14. 2-Butanol is converted into 2-methylbutanoic acid by
(a) (i) Cu, (ii) HCN, (iii) H_3O^+
(b) (i) HCN, (ii) H_3O^+
(c) (i) PCl_5, (ii) KCN, (iii) H_3O^+
(d) (i) KCN, (ii) H_3O^+

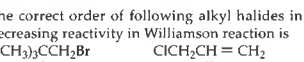
15. Which of the following has lowest solubility in water?
(a) CH_3OH (b) C_2H_5OH
(c) $(CH_3)_2CHOH$ (d) $(CH_3)_3COH$

16. What is the missing compound in the following transformation?



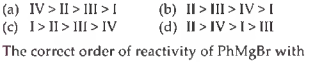
(a) $HCOOCH_3$ (b) CH_3COCH_3
(c) $CH_3COOC_2H_5$ (d)

17. The correct order of following alkyl halides in decreasing reactivity in Williamson reaction is



(a) IV > II > III > I (b) II > III > IV > I
(c) I > II > III > IV (d) II > IV > I > III

18. The correct order of reactivity of PhMgBr with



(a) I > II > III (b) III > II > I
(c) II > III > I (d) I > III > II

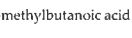
19. Which one is most reactive for addition of alcohol on carbonyl group?
(a) C_6H_5CHO (b) HCHO
(c) (d) CH_3CH_2CHO

20. Which of the following is the strongest acid?
(a) 4-Nitrobenzoic acid
(b) 4-Methylbenzoic acid
(c) 4-Methoxybenzoic acid
(d) 4-Ethylbenzoic acid

21. Identify 'Z' in the sequence :

(a) C_6H_5CN (b) $C_6H_5CONH_2$
(c) C_6H_5COOH (d) $C_6H_5CH_2NH_2$

22. Which of the reagents are not used in the preparation of anisole via Williamson's synthesis?
(a) Na (b) CH_3Cl
(c) (d)

23. X, X is
(a) 
(b)
(c) (d)

24. Decreasing order of boiling points of
(I) CH_3CH_2CHO (II) $CH_3CH_2CH_2OH$
(III) $CH_3OCH_2CH_3$ (IV) $CH_3CH_2CH_3$
(a) I > II > III > IV (b) II > I > III > IV
(c) III > II > I > IV (d) II > III > I > IV

25. Butanenitrile may be prepared by heating
(a) propyl alcohol with alc. KCN
(b) butyl alcohol with alc. KCN
(c) butyl chloride with alc. KCN
(d) propyl chloride with alc. KCN

26. Which of the following would not react with benzenesulphonyl chloride in aq. NaOH?
(a) Aniline
(b) *N*-Methylaniline
(c) *N*, *N*-Dimethylaniline
(d) Ethylamine

27. Ease of esterification of the following alcohols CH_3CH_2OH (I), $(CH_3)_2CHOH$ (II) and $(CH_3)_3COH$ (III) with HCOOH is
(a) I < II < III (b) III < II < I
(c) II < I < III (d) I = II = III

28. What are the products of the following reaction?
$C_6H_5OCH_2CH_2OH \xrightarrow[\text{heat}]{\text{excess HBr}}$
(a) $C_6H_5OH + BrCH_2CH_2Br$
(b) $C_6H_5OH + HOCH_2CH_2OH$
(c) $C_6H_5Br + HOCH_2CH_2OH$
(d) $C_6H_5OH + BrCH_2CH_2OH$

29. Ozonolysis of an organic compound gives formaldehyde as one of the products. This confirms the presence of
(a) a vinyl group (b) an isopropyl group
(c) an acetylene triple bond
(d) two ethylenic double bonds

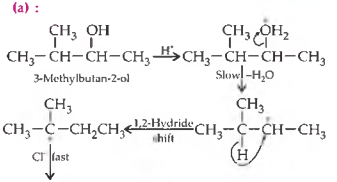
30. The product of acid catalysed hydration of 2-phenylpropene is
(a) 3-phenyl-2-propanol
(b) 1-phenyl-2-propanol
(c) 2-phenyl-2-propanol
(d) 2-phenyl-1-propanol

SOLUTIONS

1. **(c)** : Presence of an electron withdrawing groups increases the reactivity while presence of electron donating groups decreases the reactivity.

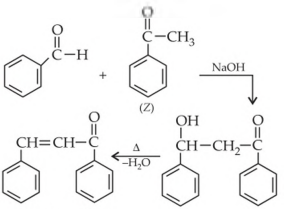
2. **(d)** : Ammonia is the weakest base.

3. **(a)** :

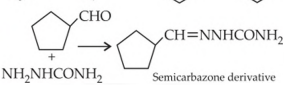


4. **(c)** : In acidic medium, coupling occurs at *ortho* position to the amino group but in basic medium, coupling occurs at *ortho* position to phenolic group.

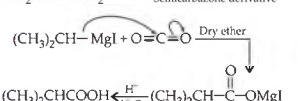
5. **(d)** :



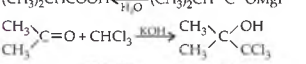
6. **(b)** :



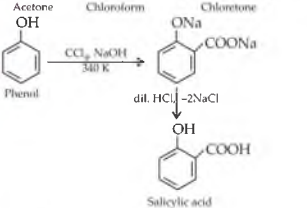
7. **(c)** :



8. **(b)** :



9. **(c)** :



10. **(d)** :

11. **(c)** : Acidity increases as the electronegativity of the carbon atom directly attached to —COOH group increases.
Benzoic acid is stronger acid than acrylic acid.

12. **(d)** : Only 1° amides undergo Hofmann bromamide degradation reaction. Since $CH_3CONHCH_3$ is a 2° amide, therefore, it does not undergo Hofmann bromamide degradation reaction.

13. **(b)** : 3° amine does not react with Hinsberg's reagent, 2° amine reacts but salt formed is not soluble in alkali.

1° amine reacts and salt formed is soluble in alkali.

$(CH_3)_2N-CH_2-CH_2-NHCH_3$

$\downarrow C_6H_5SO_2Cl$

$(CH_3)_2N-CH_2CH_2-\underset{\underset{CH_3}{|}}{N}-SO_2-C_6H_5$

Not soluble in aq. NaOH
but dissolves in sulphuric acid

14. (c) :

$CH_3-\underset{\underset{\text{2-Butanol}}{OH}}{\underset{|}{CH}}-CH_2-CH_3 + PCl_5 \downarrow$

$CH_3-\underset{\underset{Cl}{|}}{CH}-CH_2-CH_3 + POCl_3 + HCl$

$\downarrow KCN$

$CH_3-\underset{\underset{CN}{|}}{CH}-CH_2-CH_3 + KCl$

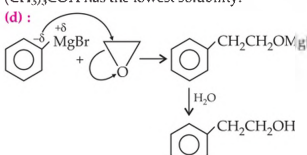
$\downarrow H_3O^+$

$CH_3-\underset{\underset{COOH}{|}}{CH}-CH_2-CH_3 + NH_3$

2-Methylbutanoic acid

15. (d) : Solubility decreases as the length of carbon chain or hydrocarbon part increases. Thus, $(CH_3)_3COH$ has the lowest solubility.

16. (d) :



17. (a) : The reactivity of alkyl halides is in the order, $CH_3 > 1° > 2° > 3°$ as tendency of alkyl halides to undergo elimination is $3° > 2° > 1°$.

C — Br bond length is longer than C — Cl. So, C — Br bond is easier to break than C — Cl bond.

$CH_2{=}CHCH_2^+$ carbocation is resonance stabilised *i.e.*, $[CH_2{=}CH{-}CH_2^+ \longleftrightarrow {}^+CH_2{-}CH{=}CH_2]$.

So, it reacts faster than *n*-propyl chloride.

(I) is least reactive because of steric hinderance of bulkier alkyl group.

18. (c) : PhMgBr reacts with a carbonyl compound and the reaction is nucleophilic addition reaction which depends upon electrophilicity and steric crowding around carbonyl group. Thus CH_3CHO is most reactive and $C_6H_5COC_6H_5$ is least reactive.

19. (b) : HCHO is highly reactive towards nucleophilic addition reactions.

20. (a) : 4-Nitrobenzoic acid is the strongest acid as $-NO_2$ group shows $-I$ and $-M$ at *ortho* and *para* positions as it is a strongest electron withdrawing group.

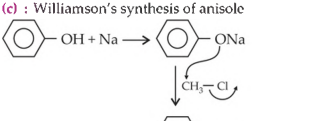
21. (c) :

$C_6H_5NH_2 \xrightarrow[275\ K]{NaNO_2 + HCl} \underset{(X)}{C_6H_5\overset{+}{N}_2Cl^-} \xrightarrow{CuCN}$

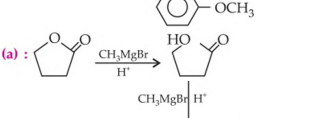
$C_6H_5COOH \xleftarrow[boil]{H^+/H_2O} C_6H_5CN$

Benzoic acid (Z) (Y)

22. (c) : Williamson's synthesis of anisole



23. (a) :



24. (b) : II > I > III > IV

25. (d) : $CH_3CH_2CH_2Cl + \text{alc. } KCN \xrightarrow{100°C} CH_3CH_2CH_2CN + KCl$

26. (c) : Primary and secondary amines react with benzenesulphonyl chloride and form HCl while tertiary amines do not give this reaction.

$RNH_2 + ClSO_2C_6H_5 \longrightarrow RNHSO_2C_6H_5 + HCl$

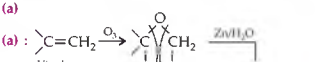
$R_2NH + ClSO_2C_6H_5 \longrightarrow R_2NSO_2C_6H_5 + HCl$

So, *N*, *N*-dimethylaniline $\left[C_6H_5-\underset{\underset{CH_3}{|}}{N}-CH_3\right]$ does not react with benzenesulphonyl chloride.

27. (b) : As the size of the alcohol increases, the ease of nucleophile attack of the alcohol on the $\diagdown C=O$ group of —COOH group decreases due to steric hindrance and hence ease of esterification decreases.

28. (a)

29. (a) :



30. (c) : Addition occurs according to Markovnikov's rule.

$CH_3-\underset{\underset{\text{2-Phenylpropene}}{Ph}}{\underset{|}{C}}=CH_2 \xrightarrow{H_2O} CH_3-\underset{\underset{\text{2-Phenyl-2-propanol}}{OH}}{\underset{|}{C}}-CH_3$

EXAMINER'S MIND NCERT CLASS XI

The questions given in this column have been prepared strictly on the basis of NCERT Chemistry for Class XI. This year JEE (Main & Advanced) / AIPMT / AIIMS/other PMTs have drawn their papers heavily from NCERT books.

HYDROCARBONS | ENVIRONMENTAL CHEMISTRY

SECTION - I

Only One Option Correct Type

This section contains 20 multiple choice questions. Each question has four choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

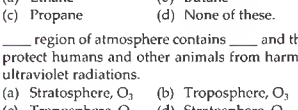
1. The maximum number of isomers for an alkane with the molecular formula C_5H_{12} is
(a) 2 (b) 5 (c) 4 (d) 3

2. Which of the following compounds cannot be prepared by Kolbe's electrolytic method?
(a) Ethane (b) Butane
(c) Propane (d) None of these.

3. ____ region of atmosphere contains ____ and thus protect humans and other animals from harmful ultraviolet radiations.
(a) Stratosphere, O_3 (b) Troposphere, O_3
(c) Troposphere, O_2 (d) Stratosphere, O_2

4. Benzene on ozonolysis gives
(a) cyclohexane (b) BHC
(c) ethanedial (d) Both (a) and (b).

5. *X*, *Y* and *Z* in the following reaction are respectively



(a) aq. KOH, $NaNH_2$, Red hot Fe tube/873 K
(b) alc. KOH, NaBr, Red hot Fe tube
(c) alc. KOH, $NaNH_2$, Red hot Fe tube/873 K
(d) aq. KOH, NaBr, Red hot Fe tube

6. The smog is essentially caused by presence of
(a) O_2 and O_3 (b) O_3 and N_2
(c) oxides of sulphur and nitrogen
(d) O_2 and N_2

7. Photochemical smog occurs in warm, dry and sunny climate. One of the following is not amongst the components of photochemical smog. Identify it.
(a) NO_2 (b) O_3
(c) SO_2
(d) Unsaturated hydrocarbons

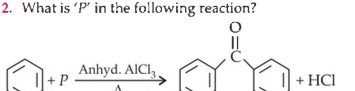
8. Ozone layer in the stratosphere is depleted by
(a) C_6Cl_6 (b) C_6H_6 (c) C_6F_6 (d) CF_2Cl_2

9. Which of the following is antiaromatic?
(a) Phenanthrene
(b) Cyclooctatetraenyl dianion
(c) Cyclopropenyl cation
(d) Cycloheptatriene

10. Propyne on passing through red hot iron tube at 873 K, gives
(a) benzene
(b) anthracene
(c) 1, 4-dimethylbenzene
(d) 1, 3, 5-trimethylbenzene

11. Dinitrogen and dioxygen are main constituents of air but these do not react with each other to form oxides of nitrogen because
(a) the reaction is endothermic and requires very high temperature
(b) the reaction can be initiated only in presence of a catalyst
(c) oxides of nitrogen are unstable
(d) N_2 and O_2 are unreactive.

12. What is '*P*' in the following reaction?

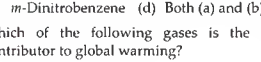


(a) CH_3COCl (b) $(CH_3CO)_2O$
(c) C_6H_5COCl (d) Both (a) and (c).

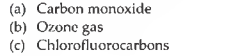
13. What product is formed on reaction of nitrobenzene with fuming nitric acid in the presence of concentrated sulphuric acid?
(a) *o*-Dinitrobenzene (b) *p*-Dinitrobenzene
(c) *m*-Dinitrobenzene (d) Both (a) and (b)

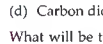
14. Which of the following gases is the major contributor to global warming?
(a) Carbon monoxide
(b) Ozone gas
(c) Chlorofluorocarbons
(d) Carbon dioxide

15. What will be the major product of the following reaction?



2-Methylpropene



(c)  (d) All of these.

16. Biochemical Oxygen Demand, (BOD) is a measure of organic material present in water. BOD value less than 5 ppm indicates a water sample to be
(a) rich in dissolved oxygen
(b) poor in dissolved oxygen
(c) highly polluted
(d) not suitable for aquatic life.

17. The atmospheric gas which cannot produce greenhouse effect is
(a) N_2 (b) H_2O (c) CO_2 (d) O_3

18. Excess of which of the following ions concentration in drinking water can cause blue baby syndrome?
(a) Lead (b) Nitrate
(c) Sulphate (d) Fluoride

19. Out of the following compounds, which is most acidic?
(a) Ethyne (b) Propane
(c) Butene (d) Propyne

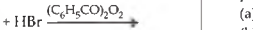
20. Fish die in water bodies polluted by sewage due to
(a) pathogens
(b) clogging of gills by slit
(c) decrease in D.O.
(d) foul smell.

SECTION - II

One or More Options Correct Type

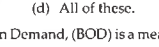
This section contains 5 multiple choice questions. Each question has four choices (a), (b), (c) and (d), out of which ONE or MORE are correct.

21. Which of the following will be the product(s) of the following reaction?



(a) Ethane (b) Butane
(c) Propane (d) Pentane

22. Which of the following conditions show the polluted environment?
(a) pH of rain water is 5.6.
(b) Amount of carbon dioxide in the atmosphere is 0.03%.
(c) Biochemical oxygen demand is 10 ppm.
(d) Eutrophication

23. Which of the following alkenes on ozonolysis give a mixture of ketones only?
(a)
(b)
(c)  (d)

24. Components of photochemical smog are
(a) oxygen (b) acrolein
(c) peroxyacetyl nitrate
(d) nitric oxide.

25. Which of the following are *o, p*-directing groups?
(a) Toluene (b) Aniline
(c) Nitrobenzene (d) Benzaldehyde

SECTION - III

Paragraph Type

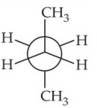
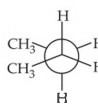
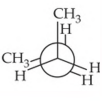
This section contains 2 paragraphs each describing theory, experiment, data, etc. Six questions relate to two paragraphs with three questions on each paragraph. Each question of a paragraph has only one correct answer among the four choices (a), (b), (c) and (d).

Paragraph for Questions 26 to 28

Rotation around a C—C single bond is not completely free. It is hindered by a small energy barrier of 1-20 kJ mol^{-1} due to weak repulsive interaction

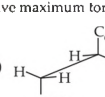
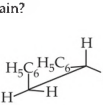
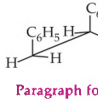
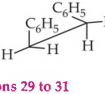
between the adjacent bonds. Such a type of repulsive interaction is called torsional strain. Conformation in which atoms attached to two carbons are as closed together as possible is called eclipsed conformation and the other in which atoms are as far apart as possible is known as the staggered conformation. Any other intermediate conformation is called a skew conformation.

26. Which of the following is the most stable conformation of *n*-butane?

(a)
(b) 
(c) 
(d) 

27. Dihedral angle in the eclipsed conformation of ethane in Newman's projection is
(a) 180° (b) 60° (c) 0° (d) 45°

28. Which of the following conformations of 1, 2-diphenylethane in Sawhorse projection, will have maximum torsional strain?

(a) 
(b) 
(c) 
(d) 

Paragraph for Questions 29 to 31

The word smog is derived from smoke and fog. This is the most common example of air pollution that occurs in many cities throughout the world. There are two types of smog:
Classical smog occurs in cool humid climate. Photochemical smog occurs in warm, dry and sunny climate. The main components of the photochemical smog result from the action of sunlight on unsaturated hydrocarbons and nitrogen oxides produced by automobiles and factories.

29. The brown, hazy fumes of photochemical smog are due to
(a) nitrogen dioxide (b) PAN formation
(c) aldehydes (d) SO_2.

30. Which of the following statements is incorrect?
(a) Classical smog is also called London smog, while photochemical smog is known as Los Angeles smog.
(b) Classical smog is formed in the months of summer, while photochemical smog is formed during winters.
(c) Classical smog is reducing in character while photochemical smog is oxidising.
(d) All are correct.

31. PAN present in the photochemical smog stands for
(a) polyacrylonitrile (b) peroxyacetyl nitrate
(c) Both (a) and (b) (d) None of these.

SECTION - IV

Matching List Type

This section contains 3 multiple choice questions. Each question has matching lists. The codes for the lists have choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

32. Match the list I with list II and select the correct answer using the code given below the lists.

List I	List II
P. $CH_3-C\equiv C-CH_3$ $\xrightarrow{\text{dil. } H_2SO_4/HgSO_4}$	1. $CH_3-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-CH_3$
Q. $CH_3-C\equiv C-CH_3$ $\xrightarrow[\text{(ii) } Zn/H_2O]{\text{(i) } O_3/CH_2Cl_2}$	2. $CH_3-\underset{\underset{OH}{\|}}{CH}-\underset{\underset{OH}{\|}}{CH}-CH_3$
R. $CH_3-CH=CH-CH_3$ $\xrightarrow[273\text{ K}]{\text{dil. } KMnO_4}$	3. $CH_3-\underset{\underset{CH_3}{\|}}{C}=O$
S. $CH_3-\underset{\underset{CH_3}{\|}}{C}=\underset{\underset{CH_3}{\|}}{C}-CH_3$ $\xrightarrow{KMnO_4/H^+}$	4. $CH_3-CH_2-\underset{\underset{O}{\|}}{C}-CH_3$

	P	Q	R	S
(a)	1	2	3	4
(b)	2	1	4	3
(c)	4	2	3	1
(d)	4	1	2	3

33. Match the activity given in list I with the type of pollution created by it given in list II.

List I (Activity)		List II (Effect)
P.	Using carbamates as pesticides	1. Water pollution
Q.	Using synthetic detergents for washing clothes	2. Photochemical smog, damage to plant life, corrosion to building material, induce breathing problems, water pollution
R.	Releasing gases produced by automobiles and factories in the atmosphere	3. Damaging ozone layer
S.	Using chlorofluorocarbon compounds for cleaning computer parts	4. May cause nerve diseases in humans

	P	Q	R	S
(a)	1	2	3	4
(b)	4	1	2	3
(c)	4	2	1	3
(d)	3	4	1	2

34. Match the list I with list II and select the correct answer using the code given below the lists.

List I		List II
P.	$CH_3CH_2Br \xrightarrow[\Delta]{\text{alc. KOH}}$	1. Dehalogenation
Q.	$C_6H_{14} \xrightarrow[\Delta]{773\ K}$	2. Dehydration
R.	$BrCH_2CH_2Br \xrightarrow{Zn}$	3. Dehydrohalogenation
S.	$CH_3CH_2OH \xrightarrow[\Delta]{\text{conc. } H_2SO_4}$	4. Pyrolysis

	P	Q	R	S
(a)	1	2	3	4
(b)	3	1	2	4
(c)	3	4	1	2
(d)	4	1	3	2

SECTION - V

Assertion-Reason Type

In the following questions, a statement of assertion is followed by a statement of reason. Mark the correct choice as :

(a) If both assertion and reason are true and reason is the correct explanation of assertion.
(b) If both assertion and reason are true but reason is not the correct explanation of assertion.
(c) If assertion is true but reason is false.
(d) If both assertion and reason are false.

35. **Assertion :** The reactivity of alkenes towards HX increases in the order:
1-phenyl-2-butene > 2-butene > 1-butene > propene.
Reason : Reactivity of HX increases with increase of number of carbon atoms.

36. **Assertion :** Greenhouse effect was observed in houses used to grow plants and these are made of transparent glass.
Reason : Greenhouse name has been given because glass houses are made of green glass.

37. **Assertion :** Toluene on Friedel — Crafts methylation gives *o*- and *p*-xylene.
Reason : $-CH_3$ group bonded to benzene ring increases electron density at *o*- and *p*-position.

38. **Assertion :** Excessive use of chlorinated synthetic pesticides causes soil and water pollution.
Reason : Such pesticides are non-biodegradable.

39. **Assertion :** 1-Butene on reaction with HBr in the presence of a peroxide produces 1-bromobutane.
Reason : It involves the formation of a primary radical.

40. **Assertion :** If the concentration of dissolved oxygen of water is above 6 ppm, the growth of aquatic life gets inhibited.
Reason : Highly polluted water has BOD value less than 5 ppm.

SECTION - VI

Integer Value Correct Type

This section contains 10 questions. The answer to each question is a single digit integer, ranging from 0 to 9 (both inclusive).

41. Maximum number of isomers for an alkene with molecular formula C_5H_{10} is

42. The number of compounds, among the following, having zero dipole moment is
Propene, 1-Butene, *cis*-But-2-ene, *trans*-But-2-ene, *trans*-Pent-2-ene, *cis*-Hex-3-ene, 2,2-Dimethylpropane, 2, 2, 3, 3-Tetramethylbutane

43. Fluoride ion concentration in drinking water above x ppm would cause brown mottling of teeth. The value of x is

44. Number of carbon atoms in alkyne having molecular mass 96 is

45. Of the following compounds, number of compounds responsible for photochemical smog is
CF_2Cl_2, Ozone, Sulphuric acid, Nitric oxide, Nitric acid, Hydrocarbons, Formaldehyde, Acrolein, PAN, Carbonic acid

46. The number of carbon atoms present in the product formed on heating sodium salt of pentanoic acid with sodalime is

47. The maximum limit of nitrate ion in drinking water is $y \times 10$ ppm. The value of y is

48. Out of the following compounds, the number of compounds that cannot be prepared by Kolbe's electrolytic method is
Ethane, Butane, Methane, Propane, Pentane, Hexane, Ethene, Ethyne

49. The layer of gas, O_x in stratosphere is called earth's protective umbrella as it protects earth's surface from the effects of harmful ultraviolet radiations. x is

50. According to international standards of drinking water, the tolerable limit of fluoride ions in water is y ppm. The value of y is

SOLUTIONS

1. **(d)**: $CH_3-CH_2-CH_2-CH_2-CH_3$
n-Pentane

$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-CH_3$
2-Methylbutane

$CH_3-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-CH_3$
2, 2-Dimethylpropane

2. **(c)**: Propane cannot be prepared by Kolbe's electrolytic method as this method is used to prepare only alkanes with even number of carbon atoms.

3. **(a)**: Ozone layer is present in stratosphere and cuts-off harmful ultraviolet radiations from reaching the earth's surface.

4. **(c)**: Benzene $\xrightarrow[Zn/H_2O]{O_3}$ 3 CHO (Glyoxal)

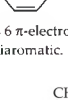
5. **(c)**

6. **(c)**: Oxides of sulphur and nitrogen are major responsible factors for smog.

7. **(c)**: The common components of photochemical smog are NO_2, O_3 and unburnt hydrocarbons.

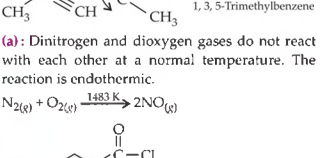
8. **(d)**: Chlorofluorocarbons(CFCs) are responsible for depletion of ozone layer.

9. **(d)**:



It has 6 π-electrons, but it is non-planar. Hence, it is antiaromatic.

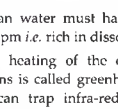
10. **(d)**:



11. **(a)**: Dinitrogen and dioxygen gases do not react with each other at a normal temperature. The reaction is endothermic.

$N_{2(g)} + O_{2(g)} \xrightarrow{1483\ K} 2NO_{(g)}$

12. **(c)**: *P* is



13. **(c)**: $-NO_2$ is a *m*-directing group.

14. **(d)**: Carbon dioxide is the major contributor to global warming.

15. **(b)**: It is anti-Markovnikov addition reaction.

16. **(a)**: Clean water must have BOD value of less than 5 ppm *i.e.* rich in dissolved oxygen.

17. **(a)**: The heating of the earth due to trapped radiations is called greenhouse effect. The gases which can trap infra-red radiations given by the sun to produce greenhouse effect leading to heating up the environment are called greenhouse gases. *e.g.* CO_2, H_2O (water vapour), and ozone (O_3).

18. **(b)**: Excess of nitrate in drinking water causes blue baby syndrome.

19. **(a)**: More the *s*-character, more will be the acidic strength. Hydrocarbons follow the acidic strength order; Alkynes (50%) > Alkenes (33%) > Alkanes (25%)
Among ethyne and propyne, ethyne is more acidic than propyne.

20. **(c)** : Microorganisms from sewage consume all dissolved oxygen and fish get deprived of this oxygen and ultimately die.

21. **(a,b,c)** : The two different alkyl halides in addition to reacting with each other, also react amongst themselves giving a mixture of three alkanes.

$$CH_3Br + 2Na + BrCH_2CH_3 \xrightarrow{\text{dry ether}} \underset{\text{Propane}}{CH_3CH_2CH_3}$$

$$CH_3Br + 2Na + BrCH_3 \xrightarrow{\text{dry ether}} \underset{\text{Ethane}}{CH_3CH_3}$$

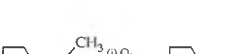
$$CH_3CH_2Br + 2Na + BrCH_2CH_3 \xrightarrow{\text{dry ether}} \underset{\text{Butane}}{CH_3CH_2CH_2CH_3}$$

22. **(c, d)** : BOD value more than 5 ppm shows water is polluted.
The process in which nutrient enriched water bodies support a dense plant population, which kills aquatic life by depriving them of oxygen and results in subsequent loss of biodiversity is known as eutrophication.

23. **(c, d)** :

$$CH_3-CH=CH-CH_3 \xrightarrow[\text{(ii) } Zn/H_2O]{\text{(i) } O_3} 2CH_3CHO$$

$$CH_3-\underset{CH_3}{CH}-CH=CH_2 \xrightarrow[\text{(ii) } Zn/H_2O]{\text{(i) } O_3} CH_3-\underset{CH_3}{CH}-CHO + HCHO$$



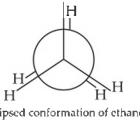
$$(CH_3)_2C=C(CH_3)_2 \xrightarrow[\text{(ii) } Zn/H_2O]{\text{(i) } O_3} 2(CH_3)_2C=O$$

24. **(b, c, d)** : Oxygen is not the component of photochemical smog.

25. **(a, b)** : Toluene and aniline are *o, p*-directing while nitrobenzene and benzaldehyde are *m*-directing groups.

26. **(b)**: The order of stability of different conformations of *n*-butane is
Staggered (Anti) > Skew or Gauche > Partially eclipsed > Fully eclipsed
The most stable conformation is anti (staggered) because two bulkier groups are far apart.

27. **(c)** :



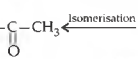
Eclipsed conformation of ethane

28. **(c)** : Fully eclipsed conformation has the maximum torsional strain.

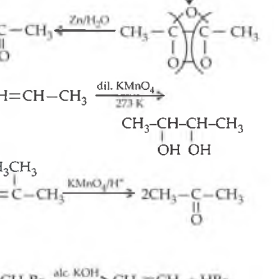
29. **(a)** : Brown hazy fumes of photochemical smog are due to nitrogen dioxide.

30. **(b)**: Classical smog is formed in winters whereas photochemical smog is formed during summer.

31. **(b)**: Peroxyacetyl nitrate



32. **(d)**:



33. **(b)**

34. **(c)** :

$$P: CH_3CH_2Br \xrightarrow[\Delta]{\text{alc. KOH}} CH_2=CH_2 + HBr$$

$$Q: C_6H_{14} \xrightarrow[\Delta]{773\ K} \begin{cases} C_6H_{12} + H_2 \\ C_4H_8 + C_2H_6 \\ C_3H_6 + C_2H_4 + CH_4 \end{cases}$$

$$R: BrCH_2CH_2Br \xrightarrow{Zn} CH_2=CH_2 + ZnBr_2$$

$$S: CH_3CH_2OH \xrightarrow{\text{conc. } H_2SO_4} CH_2=CH_2 + H_2O$$

35. **(c)** : More the electron density on the olefinic carbon, more is its reactivity towards an electrophile, hence order is
1-phenyl-2-butene > 2-butene > 1-butene > propene

36. **(c)** : Houses used to grow plants are not made up of green glasses. The glasses are transparent.

37. **(a)** : $-CH_3$ group is *ortho* and *para*-directing group.

38. **(a)**

39. **(c)** : (i) (a) $(R_2O_2) \xrightarrow{\Delta} RO^{\bullet}$

(b) $RO^{\bullet} + HBr \longrightarrow ROH + Br^{\bullet}$

(ii) (a) $CH_3CH_2CH=CH_2 + Br^{\bullet} \longrightarrow CH_3\overset{\bullet}{C}HCH_2Br$ (2° radical)

(b) $CH_3CH_2\overset{\bullet}{C}HCH_2Br + HBr \longrightarrow CH_3CH_2CH_2CH_2Br + Br^{\bullet}$

1-Bromobutane

40. **(d)**: If the concentration of dissolved oxygen of water is below 6 ppm, the growth of aquatic life gets inhibited. Highly polluted water has BOD value of 17 ppm or more.

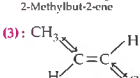
41. **(5)** : $CH_3-CH_2-CH_2-CH=CH_2$ Pent-1-ene

$CH_3-CH_2-CH=CH-CH_3$ Pent 2-ene

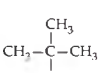
$CH_3-CH_2-C(CH_3)=CH_2$ 2-Methylbut-1-ene

$CH_3-CH(CH_3)-CH=CH_2$ 3-Methylbut-1-ene

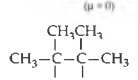
$CH_3-CH=C(CH_3)-CH_3$ 2-Methylbut-2-ene

42. **(3)** : 

trans-But-2-ene ($\mu \neq 0$)



2, 2-Dimethylpropane ($\mu = 0$)



2, 2,3,3-Tetramethylbutane ($\mu = 0$)

In *trans*-but-2-ene, the two methyl groups are in opposite directions. Dipole moments of $C-CH_3$ bonds get cancelled.

2,2-Dimethylpropane and 2, 2, 3, 3 - tetramethyl-butane both are symmetrical molecules and hence their dipole moments are zero.

43. **(2)**

44. **(7)** : General formula for alkynes is C_nH_{2n-2}.
Molecular mass of alkyne is
$12n + 1(2n - 2) = 96$
$12n + 2n - 2 = 96$
$n = 7$
Hence, the alkyne having molecular mass 96 is C_7H_{12}.

45. **(6)** : Photochemical smog contains neither smoke nor fog. It is a mixture of compounds like O_3, NO_2, PAN, hydrocarbons, aldehydes, ketones, acrolein and CO.

46. **(4)** : The reaction is decarboxylation. Sodium salts of carboxylic acids on heating with sodalime (NaOH and CaO) give alkanes containing one carbon atom less than the carboxylic acid.

$CH_3(CH_2)_3COONa + NaOH \xrightarrow[\Delta]{CaO} CH_3(CH_2)_2CH_3 + Na_2CO_3$

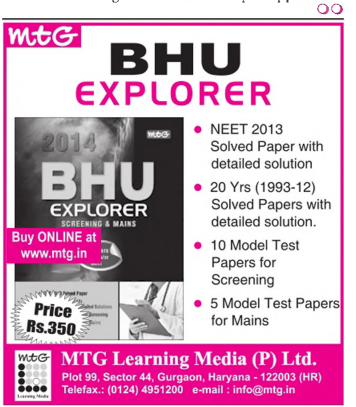
Sodium propanoate — Butane

47. **(5)** : The maximum limit of nitrate ion in drinking water is 50 ppm.

48. **(3)** : Kolbe's electrolytic method is used to prepare hydrocarbons with even number of carbon atoms.

49. **(3)** : It is ozone, (O_3) layer that protects earth's surface from harmful ultraviolet radiations.

50. **(1)** : Soluble fluoride is often added to drinking water to bring its concentration upto 1 ppm.



2014
CBSE-BOARD
CHAPTERWISE PRACTICE PAPER

Series-8

Amines | Biomolecules

Time : 3 hrs. Marks : 70

GENERAL INSTRUCTIONS

(i) All questions are compulsory.
(ii) Question numbers 1 to 8 are very short-answer questions and carry 1 mark each.
(iii) Question numbers 9 to 18 are short-answer questions and carry 2 marks each.
(iv) Question numbers 19 to 27 are also short-answer questions and carry 3 marks each.
(v) Question numbers 28 to 30 are long-answer questions and carry 5 marks each.
(vi) Use Log Tables, if necessary. Use of calculator is not allowed.

1. Write the IUPAC names of the following compounds:

(i)

(ii)

2. Complete the following reaction:
$CH_3NH_2 + CHCl_3 + KOH \longrightarrow$

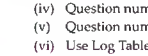
3. Name the deficiency diseases resulting from lack of vitamins C and D in the diet.

4. Name the bases present in DNA.

5. Write the structure of an amino acid which is not chiral.

6. Write the chemical equation for the following chemical reaction:
Benzenediazonium chloride is heated with fluoroboric acid.

7. Identify *X*.



8. How is the basic strength of aromatic amines affected by the presence of $-NO_2$ group on the benzene ring?

9. Write the following reactions:
(i) Gabriel phthalimide synthesis
(ii) Hoffmann bromamide reaction

10. What are essential and non-essential amino acids? Give two examples of each type.

11. Out of butan-1-amine and butan-1-ol, which is more soluble in water? Why?

12. Write the hydrolysis products of
(i) sucrose
(ii) lactose

13. How will you convert the following?
(i) Nitromethane into Dimethylamine
(ii) Methanamine into Ethanamine

14. Complete the following reactions:

(i) $CH_3(CH_2)_3CONH_2 \xrightarrow[\text{(ii) } H_2O]{\text{(i) } LiAlH_4}$

(ii) $C_6H_5NH_2 + (CH_3CO)_2O \longrightarrow$

15. Enumerate the reactions of *D*-glucose which cannot be explained by its open chain structure.

16. Arrange the following:
(i) In decreasing order of boiling point:
$(CH_3)_2NH$, CH_3NH_2, $(CH_3)_3N$

(ii) In increasing order of basic strength:
$C_6H_5NH_2$, p-$NO_2C_6H_4NH_2$, p-$CH_3C_6H_4NH_2$

OR

Arrange the following:

(i) In increasing order of basic strength:
$C_6H_5NH_2$, $C_6H_5N(CH_3)_2$, $(C_2H_5)_2NH$, CH_3NH_2

(ii) In decreasing order of basic strength in gas phase:
$C_2H_5NH_2$, $(C_2H_5)_2NH$, $(C_2H_5)_3N$, NH_3

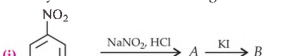
17. What is the difference between a nucleoside and a nucleotide? How are nucleotides joined together?

18. State differences between the following pairs:
(i) Reducing and non-reducing sugars
(ii) Globular and fibrous proteins

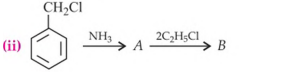
19. Do the following conversions:
(i) Aniline to p-bromoaniline
(ii) Ethanamine to ethanol
(iii) Methanamine to methyl isocyanide

20. Write the chemical reaction equations for the reactions of glucose with
(i) acetic anhydride, (ii) hydroxylamine,
(iii) bromine water.

21. Identify A and B in the following reactions:

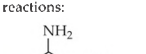
(i) 

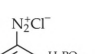
(ii)

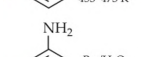
(iii) 

OR

Write the products formed in the following reactions:

(i) 

(ii) 

(iii) 

22. One day Ankit and Gaurav were playing in school playground. While playing, Ankit fell down and got injured. Blood started oozing out of his knees and did not stop. Gaurav at once rushed to his games teacher and informed her. She took Ankit to the nearby hospital immediately. Doctor gave him first aid and then suggested him to include green leafy vegetables in his diet.
(i) What values were possessed by Gaurav?
(ii) Name the vitamin (a) responsible for blood clotting, (b) present in leafy vegetables.

23. Write short notes on the following:
(i) Coupling reaction (ii) Ammonolysis

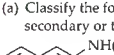
24. (i) What is a glycosidic linkage?
(ii) Define peptide linkage.
(iii) Explain the amphoteric behaviour of amino acids.

25. Give one chemical test to distinguish between the following pairs of compounds:
(i) *N*-Ethylethanamine and *N*,*N*-Diethylethanamine
(ii) Aniline and Benzylamine
(iii) Methylamine and Dimethylamine

26. (i) Name the base which is uncommon in DNA and RNA.
(ii) Write the important structural and functional differences between DNA and RNA.
(iii) The two strands in DNA are not identical but are complementary. Explain.

27. (i) How are vitamins classified? Give examples.
(ii) Name the vitamin responsible for coagulation of blood.
(iii) Name the vitamin whose deficiency causes
(a) night blindness
(b) pernicious anaemia.

28. (i) (a) Classify the following amines as primary, secondary or tertiary.



(1)

$(CH_3)_2CHNH_2$
(2)

(3)

(b) Aniline does not undergo Friedel–Crafts reaction. Explain.

(ii) (a) An aromatic compound (A) on treatment with aqueous ammonia and heating

forms compound (*B*) which on heating with Br_2 and KOH forms a compound (*C*) of molecular formula C_6H_7N. Write the structures and IUPAC names of compounds *A*, *B* and *C*.

(b) How can the acetylation of $-NH_2$ group of aniline with acetic anhydride help in preparing the monosubstituted aniline derivatives?

OR

(i) Account for the following:

(a) pK_b of aniline is more than that of methylamine.

(b) Ethylamine is soluble in water whereas aniline is not.

(ii) Complete the following series:

$$PhNH_2 \xrightarrow{A} PhN_2^+Cl^- \xrightarrow{B} PhCN \xrightarrow{C} Ph-\underset{H}{\overset{H}{C}}-NH_2$$

29. (i) Define the following terms:

(a) Anomers (b) Invert sugar

(ii) Define the three major classes of carbohydrates and give an example of each of these classes.

OR

(i) Define enzymes. Name the enzyme which converts maltose into glucose.

(ii) (a) How are proteins related to amino acids?

(b) Describe primary, secondary and tertiary structures of proteins.

(c) When is a protein said to be denatured?

30. (i) Compound (*A*) with empirical formula C_7H_9N on diazotisation gives a product which undergoes Sandmeyer's reaction with Cu_2Cl_2 and HCl to give a compound (*B*). (*B*) on oxidation gives a compound (*C*) which when heated with sodalime gives chlorobenzene. Give the structures of (*A*), (*B*), (*C*) and give the reactions.

(ii) Do the following conversions:

(a) Benzene to *N*,*N*-Dimethylaniline

(b) Ethanamine to Methanamine

OR

(i) A compound $X(C_7H_7Br)$ reacts with KCN to give $Y(C_8H_7N)$. Reduction of *Y* with $LiAlH_4$ yields $Z(C_8H_{11}N)$. *Z* gives carbylamine reaction, reacts with Hinsberg's reagent in the presence of aq. KOH to give a clear solution. What are *X*, *Y* and *Z*?

(ii) Do the following conversions:

(a) Benzene to Benzylamine

(b) Aniline to Chlorobenzene

SOLUTIONS

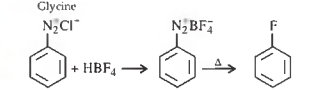
1. (i) *N*,*N*-Dimethylpropan-1-amine
   (ii) 2-Methoxyaniline

2. $CH_3NH_2 + CHCl_3 + 3KOH \longrightarrow CH_3N \rightleftharpoons C + 3KCl + 3H_2O$

3. Deficiency of vitamin C causes scurvy and deficiency of vitamin D causes rickets.

4. Adenine (A), Guanine (G), Cytosine (C) and Thymine (T)

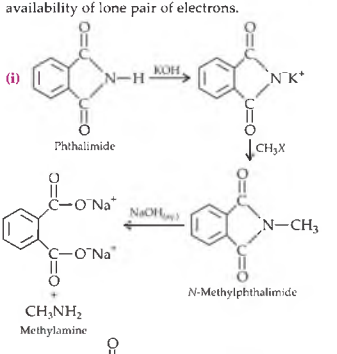
5. H_2N-CH_2-COOH
   Glycine

6. 

   Benzenediazonium chloride — Benzenediazonium fluoroborate — Fluorobenzene
   $+ BF_3 + N_2$

7. *X* is *n*-hexane, $CH_3(CH_2)_4CH_3$.

8. $-NO_2$ group is an electron withdrawing group which decreases the basic strength due to non-availability of lone pair of electrons.

9. (i) 

   (ii) $CH_3CH_2-\overset{O}{\overset{\|}{C}}-NH_2 + Br_2 + 4NaOH \longrightarrow CH_3CH_2NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$
   Propanamide — Ethylamine

10. Those amino acids which cannot be synthesised in the body and they must be obtained through diet are known as essential amino acids. *e.g.*, valine and lysine.
The amino acids, which can be synthesised in the body are known as non-essential amino acids, *e.g.*, alanine and glutamic acid.

11. Butan-1-ol is more soluble in water than butan-1-amine as alcohols are more polar due to high electronegativity of oxygen than nitrogen, they can form stronger intermolecular hydrogen bonds with water than amines.

12. **(i)** Sucrose is a disaccharide of glucose and fructose.
(ii) Lactose is a disaccharide of glucose and galactose.

13. **(i)** $CH_3NO_2 \xrightarrow{Sn/HCl} CH_3NH_2 \xrightarrow{CH_3Cl} (CH_3)_2NH$
Nitromethane; Methanamine; *N*-Methylmethanamine (Dimethylamine)

(ii) $CH_3NH_2 \xrightarrow{HNO_2} CH_3OH \xrightarrow{PCl_5} CH_3Cl \xrightarrow{KCN} CH_3CN \xrightarrow[4[H]]{Na/C_2H_5OH} CH_3CH_2NH_2$
Methanamine; Methanol; Chloromethane; Ethanenitrile; Ethanamine

14. **(i)** $CH_3(CH_2)_3CONH_2 \xrightarrow[(ii)\ H_2O]{(i)\ LiAlH_4} CH_3(CH_2)_4NH_2$
Pentanamide; Pentanamine

(ii) $C_6H_5NH_2 + (CH_3CO)_2O \longrightarrow C_6H_5NHCOCH_3 + CH_3COOH$
Aniline; Acetic anhydride; *N*-Phenylethanamide

15. **(i)** Despite having the aldehyde group, glucose does not give 2,4-DNP test, Schiff's test and it does not form the hydrogensulphite addition product with $NaHSO_3$.
(ii) The pentaacetate of glucose does not react with hydroxylamine indicating the absence of free $-CHO$ group.

16. **(i)** $CH_3NH_2 > (CH_3)_2NH > (CH_3)_3N$
Intermolecular association is more in primary amines than in secondary amines as there are two hydrogen atoms available for hydrogen bond formation in them. Tertiary amines do not have intermolecular association due to the absence of hydrogen atom for hydrogen bond formation.

(ii) $p\text{-}NO_2C_6H_4NH_2 < C_6H_5NH_2 < p\text{-}CH_3C_6H_4NH_2$
Presence of electron releasing group (like $-CH_3$) increases the basic strength while electron withdrawing group (like $-NO_2$) decreases the basic strength.

OR

(i) $C_6H_5NH_2 < C_6H_5N(CH_3)_2 < CH_3NH_2 < (C_2H_5)_2NH$
The actual basicity order in solution follows:
$2° > 1° > 3° > NH_3$
This is due to steric hindrance. 3° amine is less basic *i.e.* electron density at the nitrogen atom is increased but approach of proton to the N-atom for solvation by water molecules is hindered by the presence of three alkyl groups.
Larger the size of alkyl groups, more will be steric hindrance and hence, amine will be less basic.

(ii) $(C_2H_5)_3N > (C_2H_5)_2NH > C_2H_5NH_2 > NH_3$
In gaseous phase, the solvation effects (stabilization of the conjugate acid due to H-bonding) are absent and hence the basic strength of amines are only because of *+I* effect of the alkyl groups which follows:
3° amine > 2° amine > 1° amine > NH_3

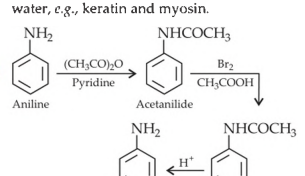
17. Nucleoside contains only two basic components of nucleic acids, *i.e.* a pentose sugar and a nitrogenous base. Nucleotide contains all the three basic components of nucleic acids, *i.e.* a phosphoric acid group, a pentose sugar and a nitrogenous base. Nucleotides are joined together by phosphodiester linkage between 5′ and 3′ carbon atoms of the pentose sugar.

18. **(i)** Those carbohydrates which reduce Fehling's solution and Tollens' reagent due to presence of free aldehydic or ketonic group are referred to as reducing sugars. All monosaccharides like glucose, fructose, galactose are reducing sugars.
Those carbohydrates which cannot reduce Fehlings' solution and Tollens' reagent because of bonded aldehydic or ketonic groups are known as non-reducing sugars. Disaccharides like sucrose is non-reducing sugar.

(ii) Globular proteins results when the polypeptide chains coil around to give three dimensional spherical shape. These are soluble in water, *e.g.*, insulin and albumins.
In fibrous proteins, polypeptide chains are

parallel and are held together by hydrogen and disulphide bonds. These are insoluble in water, *e.g.*, keratin and myosin.

19. (i)



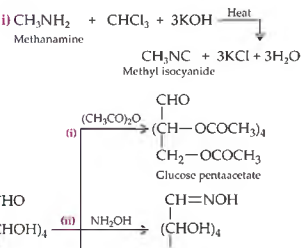
(ii) $C_2H_5NH_2 + HNO_2 \xrightarrow{NaNO_2/HCl} C_2H_5N_2^+Cl^-$ (Ethanamine)

$C_2H_5OH + N_2 + HCl \xleftarrow{H_2O}$ (Ethanol)

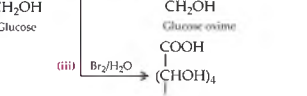
(iii) $CH_3NH_2 + CHCl_3 + 3KOH \xrightarrow{Heat}$ (Methanamine)

$CH_3NC + 3KCl + 3H_2O$ (Methyl isocyanide)

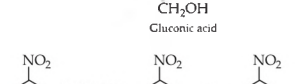
20.



21. (i)



(ii)



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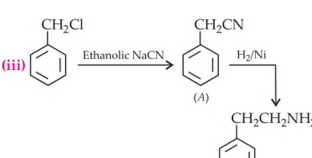
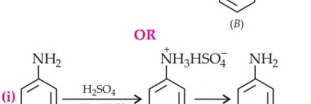
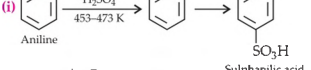


OR

(i)



(ii)



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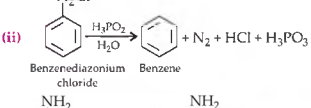
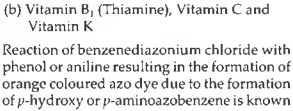


22. (i) Helping, responsible and caring nature.

(ii) (a) Vitamin K

(b) Vitamin B_1 (Thiamine), Vitamin C and Vitamin K

23. (i) Reaction of benzenediazonium chloride with phenol or aniline resulting in the formation of orange coloured azo dye due to the formation of *p*-hydroxy or *p*-aminoazobenzene is known as coupling reaction.



(ii) Reaction of alkyl halide with ethanolic solution of ammonia yields primary amines due to the replacement of halogen atom by an amino group is known as ammonolysis. Primary amine can further react with alkyl halide to form secondary amine, tertiary amine and quaternary ammonium salt.

$$CH_3Cl + NH_3 \rightarrow CH_3NH_2 \xrightarrow{CH_3Cl} (CH_3)_2NH$$

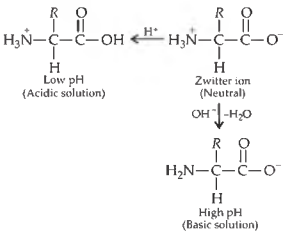
$$(CH_3)_4N^+Cl^- \xleftarrow{CH_3Cl} (CH_3)_3N \xleftarrow{CH_3Cl}$$

24. (i) The two monosaccharides are joined together by an oxide linkage formed by the loss of a water molecule. Such a linkage between two monosaccharide units through oxygen atom is called glycosidic linkage.

(ii) Peptide linkage is an amide formed between carboxyl(−COOH) group of one amino acid and amino(−NH_2) group of other amino acid with the elimination of a water molecule.

(iii) Due to the presence of −NH_2 and −COOH group within the same molecule, an inner salt is formed by internal transfer of a proton from −COOH to −NH_2 resulting in a dipolar ion, called the Zwitter ion.

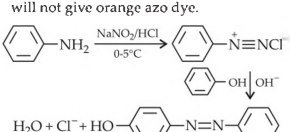
Amino acids are amphoteric in nature. They can accept or donate a proton depending on the pH of the solution.



25. (i) Add benzenesulphonyl chloride, also known as Hinsberg's reagent. Secondary amines give salt soluble in alkali whereas tertiary amines will not react.

$$C_6H_5SO_2Cl + (C_2H_5)_2NH \longrightarrow \underset{N,N\text{-Diethylbenzenesulphonamide}}{C_6H_5SO_2N(C_2H_5)_2} + HCl$$

(ii) Add nitrous acid ($NaNO_2$ + HCl) at 0-5°C. Then, add alkaline solution of phenol. Aniline will give orange azo dye whereas benzylamine will not give orange azo dye.



(iii) Methylamine (primary amine) gives carbylamine test. It gives foul odour when heated with chloroform and alcoholic KOH.

$$CH_3NH_2 + CHCl_3 + 3KOH \xrightarrow{\Delta} CH_3NC + 3KCl + 3H_2O$$

Dimethylamine (Secondary amine) does not give this test.

$$(CH_3)_2NH + CHCl_3 + 3KOH \xrightarrow{\Delta} \text{No reaction}$$

26. (i) DNA contains Thymine (T). RNA contains Uracil (U) in place of thymine.

(ii) Structural differences:

	DNA	RNA
1.	It contains deoxyribose sugar.	It contains ribose as sugar.
2.	It contains adenine, cytosine, guanine and thymine.	It contains adenine, cytosine, guanine and uracil.
3.	It forms double helix structure.	It is single stranded.

Functional differences:

DNA: For the manufacture of protein, it sends information to the cell. It undergoes self-replication.

RNA: It itself acts as a template for protein synthesis.

(iii) James Watson and Francis Crick gave a double strand helix structure for DNA. Two nucleic acid chains are wound about each other and held together by hydrogen bonds between pairs of bases. The two strands are complementary to each other because the hydrogen bonds are formed between specific pairs of bases. Adenine forms hydrogen bonds with thymine whereas cytosine forms hydrogen bonds with guanine.

27. (i) Vitamins are classified into two groups depending upon their solubility in water or fat.

Fat soluble vitamins: Vitamins which are soluble in fat and oils but insoluble in water are kept in this group. These are vitamins A, D, E and K.

Water soluble vitamins: These vitamins are soluble in water but insoluble in fat. B group vitamins and vitamin C are the examples. Water soluble vitamins must be supplied regularly in diet because they are readily excreted in urine and cannot be stored (except vitamin B_{12}) in our body.

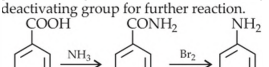
(ii) Vitamin K

(iii) (a) Vitamin A , (b) Vitamin B_{12}

25. (i) (a) 1. Secondary amine, 2. Primary amine, 3. Tertiary amine

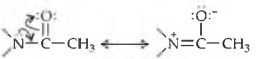
(b) Aniline does not undergo Friedel–Crafts reaction (alkylation and acetylation) due to salt formation with aluminium chloride, the Lewis acid, which is used as a catalyst. Due to this, nitrogen of aniline acquires positive charge and hence acts as a strong deactivating group for further reaction.

(ii) (a)



(A) Benzoic acid (B) Benzamide (C) Aniline

(b) The lone pair of electrons on nitrogen of acetanilide interacts with oxygen atom due to resonance as shown below:

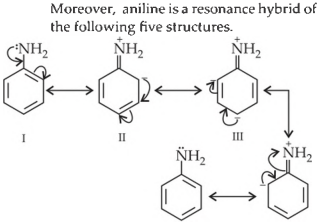


Hence, the lone pair of electrons on nitrogen is less available for donation to benzene ring by resonance. Therefore, activating effect of $-NHCOCH_3$ group is less than that of $-NH_2$ group.

OR

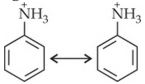
(i) (a) In case of aniline, the lone pair of electrons on the nitrogen atom is delocalized over the benzene ring. As a result, the electron density on nitrogen atom decreases. However, in methylamine, the *+I* effect of methyl group increases the electron density on the nitrogen atom. Therefore, aniline is a weaker base than methylamine. Hence, its pK_b value is higher than that of methylamine.

Moreover, aniline is a resonance hybrid of the following five structures.

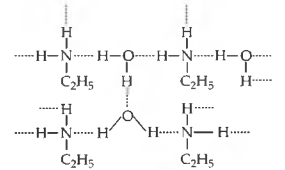


I II III IV V

Whereas, anilinium ion obtained by accepting a proton can have only two resonating structures.

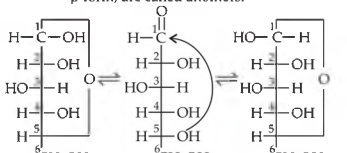


(b) As ethylamine can form hydrogen bonds with water therefore, it is soluble in water whereas aniline because of greater hydrocarbon part is less polar cannot form hydrogen bonds with water.



(ii) $PhNH_2 \xrightarrow[0\text{-}5°C]{NaNO_2/HCl} PhN_2^+Cl^- \xrightarrow{CuCN} PhCN \xrightarrow[Sn/HCl]{} PhCH_2NH_2$

29. (i) (a) The two cyclic hemiacetal forms of glucose differ only in the configuration of the hydroxyl group at C1, called anomeric carbon (the aldehyde carbon before cyclisation). Such isomers, *i.e.*, α-form and β-form, are called anomers.



α-*D*-(+)-Glucose β-*D*-(+)-Glucose

(b) Sucrose is dextrorotatory but after hydrolysis gives dextrorotatory glucose and laevorotatory fructose. Since the laevorotation of fructose (–92.4°) is more than dextrorotation of glucose (+52.5°), the mixture is laevorotatory. Thus, hydrolysis of sucrose brings about a change in the sign of rotation, from dextro (+) to laevo (–) and the product is named as invert sugar.

(ii) 1. Monosaccharides: A carbohydrate that cannot be hydrolysed further to give simpler units of polyhydroxy aldehydes or ketones, *e.g.*, glucose.

2. Oligosaccharides: Carbohydrates that yield two to ten monosaccharide units on hydrolysis. They are further classified as disaccharides, trisaccharides, tetrasaccharides, etc. depending upon the number of monosaccharides they provide on hydrolysis. *e.g.*, sucrose is a disaccharide on hydrolysis gives glucose and fructose.

3. Polysaccharides: Carbohydrates which yield a large number of monosaccharide units on hydrolysis, *e.g.*, starch.

OR

(i) Enzymes are biocatalysts which catalyse specific biochemical reactions. Maltase is an enzyme that converts maltose into glucose.

(ii) (a) Proteins are the polymers of α-amino acids and they are connected to each other by peptide bond or peptide linkage.

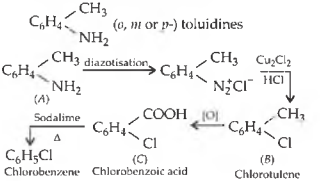
(b) Primary structure of proteins: Proteins may have one or more polypeptide chains. Each polypeptide in a protein has amino acids linked with each other in a specific sequence.

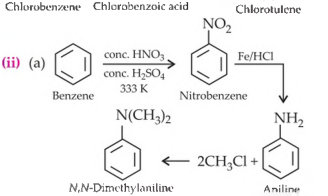
Secondary structure of proteins : It refers to the shape in which a long polypeptide chain can exist. They are found to exist in two different types of structures, α-helix and β-pleated sheet structure. These structures arise due to the regular folding of the backbone of the polypeptide chain due to hydrogen bonding between —CO— and –NH– groups of the peptide bond.

Tertiary structure of proteins: It represents overall folding of the polypeptide chains. It gives rise to two major molecular shapes, fibrous and globular.

(c) When a protein in its native form, is subjected to physical changes like change in temperature or chemical changes like change in pH, the hydrogen bonds are disturbed. Due to this, globules unfold and helix get uncoiled and protein loses its biological activity. This is called denaturation of protein.

30. (i) Since chlorobenzene is obtained from (*C*) on sodalime treatment, hence (*C*) is chlorobenzoic acid. As (*C*) is obtained from (*B*) on oxidation, considering molecular formula of (*A*), a $-CH_3$ group should be attached to benzene ring which gets oxidised to —COOH. (*B*) is obtained after diazotisation and Sandmeyer's reaction of (*A*). Therefore structure of (*A*) could be





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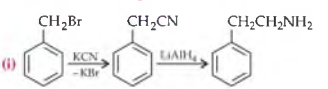
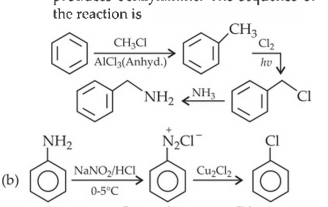


(ii) (a) Friedel—Crafts alkylation followed by reaction with halogen and ammonia produces benzylamine. The sequence of the reaction is



COMPETITION CORNER

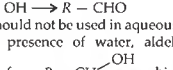
Organic Chemistry

Mukul C. Ray, Odisha

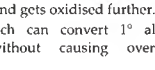
Oxidation and Reduction

Conditions and selectivity are significant in these reactions. Let us make a list of such reagents and their utility with special reference to aldehydes.

- $R-CH_2-OH \longrightarrow R-CHO$
  Reagents should not be used in aqueous medium. Because in presence of water, aldehyde gets hydrated to form $R-CH(OH)_2$ which appears as an alcohol and gets oxidised further.
- Reagents which can convert 1° alcohols to aldehydes without causing over-oxidation include:
  - PCC (pyridinium chlorochromate) in methylene chloride as solvent at 25°C.

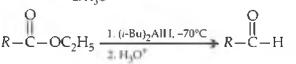


  - PDC (pyridinium dichromate) in methylene chloride as solvent at 25°C.



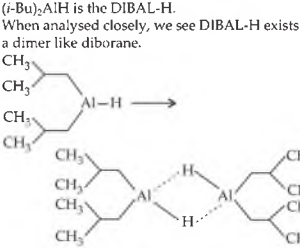
  - CrO_3 with pyridine in methylene chloride.
- Acidified $KMnO_4$ and acidified $K_2Cr_2O_7$ oxidise 1° alcohols to acids. 2° alcohols give ketones.
- Aluminium *tert*-butoxide in large excess of acetone catalyses oxidation of 2° alcohols to ketones. It is not advised in case of 1° alcohols because such strong base like *tert*-butoxide can initiate aldol condensation.

- Jone's reagent (a dilute solution of CrO_3 in dilute H_2SO_4) oxidises 2° alcohols in acetone solution at 15-20°C to give the corresponding ketones.



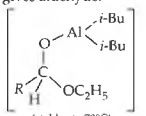
It also oxidises primary allylic alcohols to aldehydes without affecting double bond.

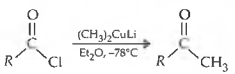
- A number of other compounds on reduction also yield aldehydes or ketones.



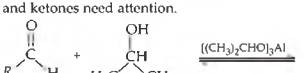
$(i\text{-}Bu)_2AlH$ is the DIBAL-H.
When analysed closely, we see DIBAL-H exists as a dimer like diborane.

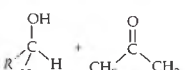
On reaction with ester it forms an intermediate, which is stable at –70°C, when separated and hydrolysed it gives aldehyde.





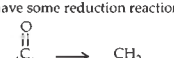
- Few reduction reactions observed on aldehydes and ketones need attention.





This is called Meerwein-Ponndorf-Verley reduction. The by-product acetone is continuously distilled off to drive the reaction towards completion.

- Again, we have some reduction reactions where

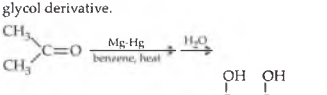


When the reagent is Zn-Hg, conc. HCl/Δ, the name is Clemmensen reduction.

When the reagent is NH_2-NH_2 followed by KOH in diglyme as solvent at 200°C, the name of the reaction is Wolff–Kishner reduction.

Another alternative is Mozingo method where $HS-CH_2-CH_2-SH$ is used in acidic medium followed by reduction using H_2/Ni.

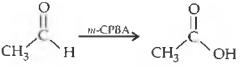
- Bimolecular reduction reaction of ketone forms glycol derivative.

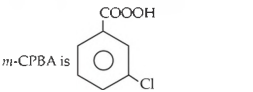


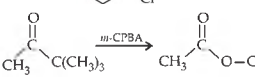
- Baeyer–Villiger oxidation in case of ketones gives esters. In case of unsymmetrical ketones, insert an oxygen atom next to the group that has higher migrating aptitude in Baeyer–Villiger oxidation. The migrating aptitude changes as:

–H > *t*-alkyl > *s*-alkyl > phenyl > *n*-alkyl > methyl

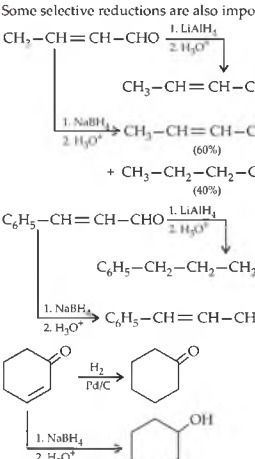
–H on the top indicates aldehyde on oxidation gives acid.



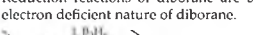




- Some selective reductions are also important.

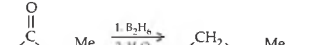


- Reduction reactions of diborane are because of electron deficient nature of diborane.

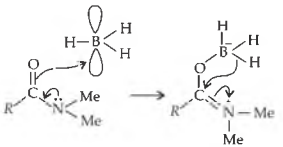


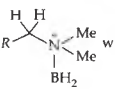
Diborane binds to electron-rich oxygen which then transfers hydride to carbonyl-carbon.

Few related reduction reactions of diborane are:

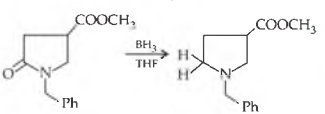


It starts with

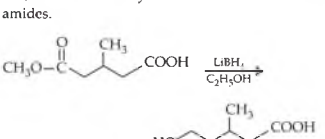


and so on to give  which is then hydrolysed.

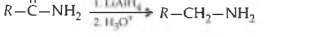
The notable point is that BH_4^- is nucleophilic but B_2H_6 is electrophilic. That is the reason why – COCl which is otherwise most easily reduced is not even touched by diborane. Even ester reacts with diborane slowly.



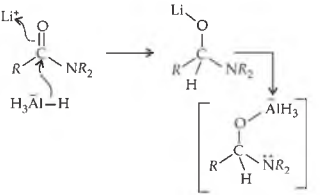
- $LiBH_4$ in alcoholic solution will reduce ester. In fact, it has selectivity for ester over acids and amides.



$LiAlH_4$ does not have this selective property. Amide is reduced by $LiAlH_4$ to form amine.

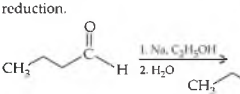


However, at 0°C if the intermediate is trapped and hydrolysed subsequently, amide can give aldehyde on its reaction with $LiAlH_4$.

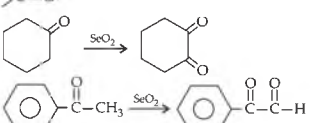


This may be trapped at 0°C

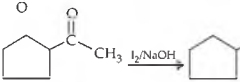
- Aldehydes, ketones or esters on treatment with Na and C_2H_5OH give primary and secondary alcohols. This is called Bouveault-Blanc reduction.



- Acids, esters and amides are not catalytically reduced. Under special condition though acid can be reduced to alkane using H_2 and heterogeneous catalyst.
- SeO_2 oxidises $-CH_2-$ group adjacent to $>C=O$.



- Tollen's reagent, Fehling's solution and Benedict's solution oxidise aldehyde to acid but they cannot oxidise ketone.
- I_2/NaOH (or Cl_2/NaOH or Br_2/NaOH) oxidises $-\underset{\underset{O}{\|}}{C}-CH_3$ or $-\underset{\underset{OH}{|}}{CH}-CH_3$ segment to $-\underset{\underset{O}{\|}}{C}-\bar{O}Na^+$ with the release of iodoform.



Also, $-\underset{\underset{O}{\|}}{C}-CH_3$ segment can be oxidised using I_2/NH_4OH but not $-\underset{\underset{OH}{|}}{CH}-CH_3$.

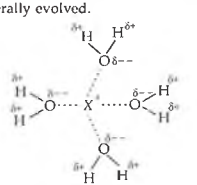
CONCEPT BOOSTER

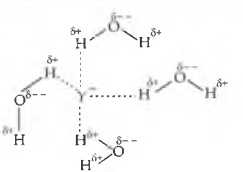
Dear students, second part of Thermodynamics is here. Few practice problems are also incorporated here. In the next issue remaining topics along with a new series will be presented. Wish you all a very happy new year. Stay well, keep yourself healthy. Take care.

*Arunava Sarkar

Different Types of Enthalpies

- **Enthalpy of solution ($\Delta_{sol}H$)**
  When 1 mole of a substance is dissolved in a particular suitable solvent then whatever amount of heat either evolved or absorbed is known as enthalpy of solution ($\Delta_{sol}H$). So, it will also have the unit of J mol^{-1} or kJ mol^{-1}.
  It is really not possible to know for each reaction whether it will be endothermic or exothermic however, we generally find that
  (i) hydrated salts absorb heat ($\Delta H_{sol} > 0$) while dissolving in suitable solvent.
  e.g. $CuSO_4{\cdot}5H_2O$
  (ii) In general, the anhydrous form of the hydrated salt evolves heat ($\Delta H_{sol} < 0$) while dissolving in suitable solvent.
  e.g. $CuSO_4$ itself.
  (iii) Salts which do not form hydrate at all have $\Delta H_{sol} > 0$.
- **Lattice enthalpy ($\Delta_{latt}H$)**
  When a salt is dissolved in solvent, the first step is that the salt breaks down into its ions for which whatever energy has to be supplied is known as lattice enthalpy ($\Delta_{latt}H$).
  In the next step, the ions are surrounded by the solvent molecules (like water). For this energy is generally evolved.





Hydration of ions

So, we have

$$XY_{(s)} \xrightarrow{\Delta_{lattice}H} X^+_{(g)} + Y^-_{(g)}$$

$$X^+_{(g)} \xrightarrow[\Delta_{hyd}H]{H_2O} X^+_{(aq)} + Y^-_{(aq)}$$

So, $XY \xrightarrow{\Delta_{sol}H} X^+_{(aq)} + Y^-_{(aq)}$

$\Delta_{latt}H$ and $\Delta_{hyd}H$ to $X^+_{(g)} + Y^-_{(g)}$

So, $\Delta_{sol}H = \Delta_{latt}H + \Delta_{hyd}H$

Enthalpy of solution ($\Delta_{sol}H$) as a function of lattice enthalpy ($\Delta_{latt}H$) and enthalpy of hydration ($\Delta_{hyd}H$)

In this regard, we must mention that if $\Delta_{latt}H > \Delta_{hyd}H$ then the dissolution of the salt becomes tough as we have to supply large amount of energy to break down the salt into its ions, so overall ΔH_{sol} becomes greater than zero and the process becomes unfavourable (you will learn this in Gibbs free energy concept to be discussed shortly). For this type of salt, with the increase in the temperature solubility of the salt increases.

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Born–Haber Cycle

It is quite tough to calculate lattice enthalpy directly (specially at the early age of 20th century). For the purpose of calculation of lattice enthalpy, at that time Max Born and Fritz Haber proposed the method to calculate lattice enthalpy. The illustration of Born–Haber cycle is very popular with the example of NaCl.

Enthalpy of formation ($\Delta_f H$) of NaCl must be known as per the following reaction:

$$Na_{(s)} + \frac{1}{2}Cl_{2(g)} \longrightarrow NaCl_{(s)};\ \Delta_f H \text{ (one mole)}$$

Steps to form $NaCl_{(s)}$ (for one mole)

(1) $Na_{(s)} \xrightarrow{\Delta_{sub}H} Na_{(g)}$

[$\Delta_{sub}H$ = enthalpy of sublimation]

(2) $Na_{(g)} \xrightarrow{I.E.} Na^+_{(g)} + e^-_{(g)}$

[$I.E.$ = ionisation energy]

(3) $\frac{1}{2}Cl_{2(g)} \xrightarrow{\frac{1}{2}\Delta_{diss}H} Cl_{(g)}$

[$\Delta_{diss}H$ = dissociation enthalpy]

(4) $Cl_{(g)} + e^-_{(g)} \xrightarrow{\Delta_{eg}H} Cl^-_{(g)}$

[$\Delta_{eg}H$ = electron gain enthalpy]

(5) $Na^+_{(g)} + Cl^-_{(g)} \xrightarrow{U} NaCl_{(s)}$

[U = lattice enthalpy]

So, eventually 1 mole $NaCl_{(s)}$ is formed and total enthalpy involved here must be equal to $\Delta_f H$.

$$\therefore\ \Delta_f H = \Delta_{sub}H + I.E. + \frac{1}{2}\Delta_{diss}H + \Delta_{eg}H + U$$

If all the values are known then easily U can be found.

Enthalpy of atomisation ($\Delta_{atom}H$)

Of course it is the enthalpy change associated with the process of breaking down one mole of a substance into its constituent atoms which are formed in the gaseous state.

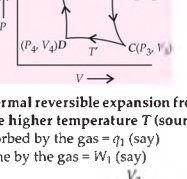
e.g. $C_2H_{6(g)} \rightarrow 2C_{(g)} + 6H_{(g)}$

Students, do remember that whatever enthalpy you get the name itself will suggest what kind of enthalpy it is. For example, $\Delta_{fus}H$ is enthalpy of fusion and of course it is related to fusion of a solid into its liquid state (other parameters like one mole, melting at melting point should be mentioned). Take a try to know about the following enthalpies.

(i) Enthalpy of vaporisation ($\Delta_{vap}H$)
(ii) Enthalpy of ionisation ($\Delta_{ion}H$)
(iii) Enthalpy of reaction ($\Delta_r H$)
(iv) Enthalpy of hydrogenation ($\Delta_{hydro}H$)

CARNOT CYCLE : AN OVERVIEW OF THERMODYNAMIC PROCESS

In the cyclic process, one mole of an ideal gas in the frictionless piston was taken for the processes assumed to be held reversibly. The steps are described below:



Step I : Isothermal reversible expansion from volume V_1 to V_2 at the higher temperature T (source):

The heat absorbed by the gas = q_1 (say)

The work done by the gas = W_1 (say)

$$= RT\ln\frac{V_2}{V_1} \quad (\because \text{1 mole gas})$$

As the gas is ideal, $\Delta U_1 = 0$

From the first law of thermodynamics,

$$q_1 = W_1 = RT\ln\frac{V_2}{V_1} \quad (\because \Delta U_1 = 0)$$

Step II : Adiabatically reversible expansion from volume V_2 to V_3:

Temperature of the gas changes from T to T'. Since, the process is adiabatic therefore heat absorbed by the gas = $q_2 = 0$.

$$\therefore\ \Delta U_2 = C_V(T' - T) \qquad [\because\ \Delta U = nC_V\,dT]$$

From the first law of thermodynamics,

$$W_2 = -\Delta U_2 = C_V(T - T')$$

(where C_V is the heat capacity of the gas at constant volume)

Step III : Isothermal reversible compression from volume V_3 to V_4 at the temperature T' (sink):

Since the gas is ideal, therefore, $\Delta U_3 = 0$

So, from the first law of thermodynamics,

$$q_3 = W_3 = RT'\ln\frac{V_4}{V_3}$$

where q_3 is the heat rejected to the sink.

Step IV : Adiabatic reversible compression from V_4 to V_1:

Temperature of the gas changes from T' to T. Since, the process is adiabatic, so $q_4 = 0$.

$$\therefore\ \Delta U_4 = C_V(T - T')$$

From the first law of thermodynamics,

$$W_4 = -\Delta U_4 = C_V(T' - T)$$

$\therefore$ Total work = $W = W_1 + W_2 + W_3 + W_4$

$$\therefore\ W = RT\ln\frac{V_2}{V_1} + C_V(T - T') + RT'\ln\frac{V_4}{V_3} + C_V(T' - T)$$

$$\Rightarrow W = RT\ln\frac{V_2}{V_1} + C_V\cancel{(T-T')} + RT'\ln\frac{V_4}{V_3} - C_V\cancel{(T-T')}$$

$$\Rightarrow W = RT\ln\frac{V_2}{V_1} - RT'\ln\frac{V_3}{V_4} \quad \text{... (i)}$$

Now, by considering the adiabatic reversible changes from B to C and D to A,

$$TV_2^{\gamma-1} = T'V_3^{\gamma-1} \text{ and } TV_1^{\gamma-1} = T'V_4^{\gamma-1}$$

$$\Rightarrow \left(\frac{V_2}{V_1}\right)^{\gamma-1} = \left(\frac{V_3}{V_4}\right)^{\gamma-1} \quad \therefore \frac{V_2}{V_1} = \frac{V_3}{V_4}$$

Putting this value in equation (i), we get

$$W = RT\ln\frac{V_2}{V_1} - RT'\ln\frac{V_2}{V_1}$$

$$\Rightarrow W = R\ln\frac{V_2}{V_1}(T-T') \quad \text{... (ii)}$$

Therefore, efficiency of the engine is

$$\eta = \frac{\text{Net work obtained}}{\text{Heat absorbed}}$$

$$\Rightarrow \eta = \frac{R(T-T')\ln(V_2/V_1)}{RT\ln(V_2/V_1)} = \frac{T-T'}{T}$$

$$\therefore \eta = \frac{W}{q_1} = \left(1-\frac{T'}{T}\right) = \frac{T-T'}{T} = \frac{\Delta T}{T}$$

$$\therefore W = q_1 \cdot \frac{\Delta T}{T}$$

This is the mathematical form of second law of thermodynamics. This relation expresses the maximum amount of work obtainable when heat is flowing from T to T'. You also observe that,

Net internal energy change involved in the cycle

$= \Delta U = \Delta U_1 + \Delta U_2 + \Delta U_3 + \Delta U_3$

$\Rightarrow \Delta U = 0 + C_V(T'-T) + 0 + C_V(T-T')$

$\Rightarrow \Delta U = 0$

Add to your Knowledge

1. Only $\frac{\Delta T}{T}$ fraction of the total quantity of heat taken from the source (high energy reservoir) can be transformed into work.
2. The efficiency of the engine $(\eta) = \frac{T-T'}{T}$ depends only on the temperature of the source and the sink and is independent of the working substance of the engine provided it is reversible *i.e.* this relation is valid for all substances *e.g.* ideal gas, real gas, solid, liquid, etc.
3. The whole of heat supplied *i.e.* q_1 will be transformed into work; $W = q_1$ only when $T' = 0$. So the engine should work between absolute zero and a higher temperature.

Since, this cannot be realized in practice, complete conversion of heat into work for a cyclic process is impossible.

4. When $T = T'$ *i.e.* the temperature of the source and the sink are the same ; $W = 0$. That is no work will be obtained by operating the engine under isothermal condition.

Statements of the Carnot Theorem

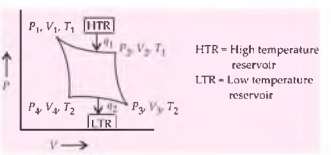
Two very important statements of Carnot theorem may be stated as follows:

- A reversible engine is more efficient than an irreversible engine.
- All reversible engines are equally efficient in working between the same temperature limits.

Kelvin—Plank Statement

This law states that "heat cannot be converted completely into work in a cyclic process that is without changing the state of any other body."

CONCEPT OF ENTROPY



We know from the Carnot cycle that the efficiency of an engine can be written as,

$$\eta = \frac{W}{q} = \frac{q_1 - q_2}{q_1} = \frac{T_1 - T_2}{T_1}$$

$$\Rightarrow \frac{q_1 - q_2}{q_1} = \frac{T_1 - T_2}{T_1} \Rightarrow 1 - \frac{q_2}{q_1} = 1 - \frac{T_2}{T_1}$$

$$\Rightarrow \frac{q_2}{q_1} = \frac{T_2}{T_1} \quad \therefore \frac{q_1}{T_1} = \frac{q_2}{T_2} \quad \text{...(i)}$$

Therefore, $\frac{q}{T}$ is constant.

Here, q is the reversible heat change at a temperature T. Again, from equation (i), we can write

$$\frac{q_1}{T_1} - \frac{q_2}{T_2} = 0$$

Here, q_1 is the heat absorbed at temperature T_1

q_2 is the heat rejected at temperature T_2

Here, $-q_2$ means that heat absorbed. So we may write

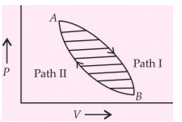
$$\frac{q_1}{T_1} + \frac{q_2}{T_2} = 0$$

So, for the Carnot cycle,

$$\sum \frac{\text{Total heat absorbed reversibly}}{\text{Temperature at which absorption takes place}} = 0$$

$$\Rightarrow \sum \frac{dq_{rev}}{T} = 0$$

Now, if we consider a cyclic process ABA, then its total $\frac{dq_{rev}}{T}$ terms can be calculated assuming that a whole cycle is made up of a large number of Carnot cycles.



Now, for all the cycles, $\sum \frac{dq_{rev}}{T} = 0$ is valid.

Now, for this complete cycle performing in two steps, *i.e.* from A to B and from B to A

$$\sum \frac{dq}{T} = \sum_{A \to B} \frac{dq}{T} + \sum_{B \to A} \frac{dq}{T}$$

If the small Carnot cycles are very large in numbers then the '$\sum$' sign may be replaced by '$\int$' sign. Then we may write

$$\sum \frac{dq}{T} = \int_A^B \frac{dq}{T} + \int_B^A \frac{dq}{T} = 0$$

The integral $\int_A^B \frac{dq}{T}$ is the summation of all the $\frac{dq}{T}$ terms when the system changes from A to B along path I and $\int_B^A \frac{dq}{T}$ is the summation of all the $\frac{dq}{T}$ terms when the system changes from B to A along the path II.

So, from above equation, we may write

$$\int_A^B \frac{dq}{T} = -\int_B^A \frac{dq}{T}$$

or $$\int_A^B \frac{dq}{T} \text{ (path I)} = \int_A^B \frac{dq}{T} \text{ (path II)}$$

Therefore, from this equation it may be concluded that $\int_A^B \frac{dq}{T}$ is a definite quantity and independent on the path followed for the change and depends only upon the initial and final states of the system.

Though, 'dq' is an inexact differential, and depends on the path followed by the system but $\frac{dq}{T}$ is such a quantity which is independent on the path or it may be considered as an exact differential. Thus $\frac{dq}{T}$ is replaced by 'dS' where 'S' is a state function and was named as '*entropy*'. Therefore, change in entropy in infinitesimal quantities can be written as

$$dS = \frac{dq_{rev}}{T} \left[i.e.\ S = \frac{q_{rev}}{T} \right]$$

Finite change in entropy can be written as

$$\Delta S = S_2 - S_1 = \frac{q_{rev}}{T}$$

Like other state functions, H, U etc., 'S' is also an extensive property and the dimension of entropy is

$$= \frac{\text{Dimension of energy}}{\text{Dimension of temperature}} = \frac{ML^2T^{-2}}{[\theta]}$$

$$= ML^2T^{-2}\theta^{-1}$$

Entropy Change for an Ideal Gas

- **Temperature and volume variation:**

It is possible to express the entropy of an ideal gas from the first law of thermodynamics.

$$dq_{rev} = dU + PdV$$

$$\Rightarrow dq_{rev} = nC_V dT + \frac{nRT}{V} dV$$

$$\left(\because PV = nRT \Rightarrow P = \frac{nRT}{V} \right)$$

Dividing both sides by T,

$$\frac{dq_{rev}}{T} = nC_V \frac{dT}{T} + nR \frac{dV}{V}$$

From definition of entropy, $dq = \frac{dq_{rev}}{T}$

$$\therefore \quad dq = nC_V \frac{dT}{T} + nR \frac{dV}{V}$$

$$= nC_V d\ln T + nR\, d\ln V$$

$$\therefore \quad \int dq = nC_V \int d\ln T + nR \int d\ln V$$

$$\Rightarrow S = nC_V \ln T + nR \ln V + I$$

[I = integral constant]

For a finite change of temperature from T_1 to T_2 and the corresponding volume change from V_1 to V_2.

$$S_1 = nC_V \ln T_1 + nR \ln V_1 + I$$

$$S_2 = nC_V \ln T_2 + nR \ln V_2 + I$$

$$\therefore \quad \Delta S = S_2 - S_1 = nC_V \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$$

$$\therefore \quad \Delta S = nC_V \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1} \qquad \text{... (i)}$$

This is the expression when both the volume and the temperature of an ideal gas are changed.

For an isothermal change in volume, the entropy change is given by the relation,

$$\Delta S = nR\ln\frac{V_2}{V_1} \quad \text{... (ii)}$$

(Since, for an isothermal process, $T_1 = T_2$).

- **Temperature and pressure variation:**

For an ideal gas, $\frac{V_2}{V_1} = \frac{P_1T_2}{P_2T_1}$

Putting this value in eqn. (i), we get

$$\Delta S = nC_V\ln\frac{T_2}{T_1} + nR\ln\frac{P_1T_2}{P_2T_1}$$

$$\Rightarrow \Delta S = nC_V\ln\frac{T_2}{T_1} + nR\ln\frac{P_1}{P_2} + nR\ln\frac{T_2}{T_1}$$

$$\Rightarrow \Delta S = n(C_V + R)\ln\frac{T_2}{T_1} + nR\ln\frac{P_1}{P_2}$$

$$\Rightarrow \Delta S = nC_p\ln\frac{T_2}{T_1} + nR\ln\frac{P_1}{P_2} \quad (\because C_V + R = C_p)$$

$$\therefore \Delta S = nC_p\ln\frac{T_2}{T_1} + nR\ln\frac{P_1}{P_2} \quad \text{... (iii)}$$

This is the expression for the change of entropy of an ideal gas when both its pressure and temperature are changed.

- **Entropy changes of an ideal gas in different processes:**

(i) Isothermal process

$T_1 = T_2$

From eqn. (i) and (iii), we get

$$\Delta S = nR\ln\frac{V_2}{V_1} = nR\ln\frac{P_1}{P_2}$$

(ii) Isobaric process

$P_1 = P_2$

From eqn. (iii), $\Delta S = nC_p\ln\frac{T_2}{T_1}$

(iii)Isochoric process

$V_1 = V_2$

From eqn. (i), we get

$$\Delta S = nC_V\ln\frac{T_2}{T_1}$$

- **Entropy change in isothermal expansion or compression of an ideal gas:**

In this section, we derive expression for the change in total entropy (system + surroundings) when an ideal gas undergoes isothermal expansion or compression process.

The change of entropy of n mole of an ideal gas is given by

$$\Delta S_{sys} = nR\ln\frac{V_2}{V_1}$$

where, V_2 = final volume

V_1 = initial volume

Reversible case : If the expansion is carried out reversibly, then $q_{rev} = W = nRT\ln\frac{V_2}{V_1}$

$$\therefore \Delta S_{sys} = \frac{q_{rev}}{T} = nR\ln\frac{V_2}{V_1}$$

where q_{rev} is heat exchange reversibly between the system and surroundings at temperature T.

It is obvious that $\Delta S_{surr} = -\frac{q_{rev}}{T}$.

Thus, $\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr}$

$$= \frac{q_{rev}}{T} - \frac{q_{rev}}{T} = 0$$

$\therefore \Delta S_{total} = 0$ for reversible process.

Irreversible case :

(a) Free expansion : The gas expands into a vacuum for this process.

$W = 0$; $q = 0$

Since, entropy is a state function, the entropy change of a system is going from a volume V_1 to volume V_2 by any path will be the same as that of a reversible change.

$$\Delta S_{sys} = \frac{q_{rev}}{T} = nR\ln\frac{V_2}{V_1}$$

Since, no heat is supplied by the surroundings, the entropy change of the surroundings would be zero.

$$\therefore \Delta S_{total} = \Delta S_{sys} + \Delta S_{surr} = nR\ln\frac{V_2}{V_1} + 0 = +ve$$

$$\left[\because V_2 > V_1. \quad \therefore nR\ln\frac{V_2}{V_1} > 0\right]$$

(b) Intermediate expansion : Since, ΔS_{sys} is the same as that of reversible change, so,

$$\Delta S_{sys} = \frac{q_{rev}}{T} = nR\ln\frac{V_2}{V_1}$$

where q_{rev} is the amount of heat absorbed by the system if the process is carried out reversibly. In the present case, the expansion is done against a constant pressure.

Thus, $q_{irrev} = -W = P_{opp}(V_2 - V_1)$

(P_{opp} = opposing pressure)

The change in entropy of the surroundings,

$$\Delta S_{surr} = -\frac{q_{irrev}}{T} = -\frac{P_{opp}(V_2 - V_1)}{T}$$

Since, $q_{rev} > q_{irrev}$

$$\therefore \Delta S_{total} = \Delta S_{sys} + \Delta S_{surr} = \frac{q_{rev}}{T} - \frac{q_{irrev}}{T} = +ve$$

Add to your Knowledge

Entropy of mixing (ΔS_{mix}) $= -nR \sum x \ln x$

n = total number of moles mixed together

x = mole fraction of each component which is mixed.

EVALUATE YOURSELF

(Single Option Correct)

1. The heats of combustion of C_nH_{2n+2}, carbon and hydrogen are a, b and c calories respectively. What will be the heat of formation of C_nH_{2n+2}?

(a) $(na + nc) - (a + b)$

(b) $(nb + nc) + (c - a)$

(c) $na + nb + nc$ (d) $\left(\frac{na + nb}{2}\right) - nc$

Sol.: Given :

(i) $C_nH_{2n+2} + \left(\frac{3n+1}{2}\right)O_2 \rightarrow nCO_2 + (n+1)H_2O$; $\Delta H_1 = a$

(ii) $C + O_2 \rightarrow CO_2$; $\Delta H_2 = b$

(iii) $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$; $\Delta H_3 = c$

Desired equation :

$nC + (n+1)H_2 \rightarrow C_nH_{2n+2}$; $\Delta H = ?$

To get the desired equation, following operation has to be done.

[(ii) × n] + [(iii) × $(n+1)$] + [reverse of (i)]

$$nC + n\cancel{O_2} + (n+1)H_2 + \cancel{\left(\frac{n+1}{2}\right)O_2} \rightarrow n\cancel{CO_2} + \cancel{(n+1)H_2O}$$

$$+ n\cancel{CO_2} + \cancel{(n+1)H_2O} \rightarrow C_nH_{2n+2} + \cancel{\left(\frac{3n+1}{2}\right)O_2}$$

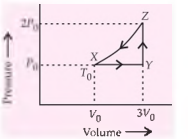
$$nC + (n+1)H_2 \rightarrow C_nH_{2n+2}$$

$\therefore \Delta H = n \cdot \Delta H_2 + (n+1) \cdot \Delta H_3 + (-\Delta H_1)$

$= nb + (n+1)c - a = (nb + nc) + (c - a)$

$\therefore$ Correct option is (b).

2. 2 moles of an ideal monoatomic gas undergoes the cyclic process as shown in the figure. What will be the change in internal energy when the gas expands from X to Z through the path XYZ?



(a) $10RT_0$ (b) $5RT_0$

(c) $2RT_0$ (d) $15RT_0$

Sol.: Problem solving strategy

Internal energy change $\Delta U = nC_V\,dT$.

Also, $PV = nRT$ or $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$

No. of moles (n) = 2

At X, $P_0V_0 = 2RT_0$ $\therefore$ $T_0 = \frac{P_0V_0}{2R}$

At Y, $P_0 \cdot 3V_0 = 2RT_Y$ $\therefore$ $T_Y = \frac{3}{2}\frac{P_0V_0}{R} = 3T_0$

At Z, $2P_0 \cdot 3V_0 = 2RT_Z$ $\therefore$ $T_Z = 6 \cdot \frac{P_0V_0}{2R} = 6T_0$

Now, change in internal energy $= nC_V\,dT$

For monoatomic gas, $C_V = \frac{3}{2}R$

$\therefore$ For the path XY

Internal energy change (ΔU_1)

$$= 2 \cdot \frac{3}{2}R(3T_0 - T_0) = 6RT_0$$

For the path YZ

Internal energy change (ΔU_2)

$$= 2 \cdot \frac{3}{2}R(6T_0 - 3T_0) = 9RT_0$$

$\therefore$ Total internal energy change

$= (6RT_0 + 9RT_0)$

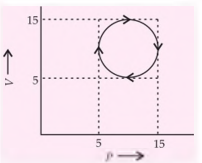
$= 15RT_0$

$\therefore$ Option (d) is correct.

3. What should be the amount of heat absorbed in this cyclic process?

(a) 5π J (b) 15π J

(c) 25π J (d) 10π J



Sol.: Problem solving strategy

Cyclic process means, internal energy change = 0.

Now, finding the work done, we may calculate the heat absorbed.

$\therefore \quad \Delta U = \Delta q + \Delta W \quad \Rightarrow \quad \Delta q = -\Delta W$

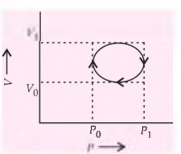
Area under a curve gives the amount of work done.

$\therefore$ Here area of the circle is

$$\pi \cdot \left(\frac{15-5}{2}\right)^2 \text{ J} = \pi \cdot 5^2 \text{ J} = 25\pi \text{ J}$$

$\therefore$ Option (c) is correct.

4. What is the amount of work done?



(a) $\frac{\pi}{4}(P_1 - P_0)(V_1 - V_0)$

(b) $\pi\left(\frac{P_1 - P_0}{2}\right)^2$

(c) $\pi\left(\frac{V_1 - V_0}{2}\right)^2$

(d) None of these.

Sol.: The idea of giving this problem is of course to correlate with the previous problem. Look the difference carefully. In the earlier case $(P_f - P_i)$ and $(V_f - V_i)$ were equal in magnitude. Hence it was easy to understand that the diagram was a circle and area is πr^2. But here, we do not know whether $(P_1 - P_0)$ is equal to $(V_1 - V_0)$ or not. Hence, in general consider it as an ellipse.

$$\text{Area of ellipse} = \pi \cdot \left(\frac{P_1 - P_0}{2}\right) \cdot \left(\frac{V_1 - V_0}{2}\right)$$

$$= \frac{\pi}{4}(P_1 - P_0)(V_1 - V_0)$$

$\therefore$ Option (a) is correct.

EXAM ALERT!

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CHEMISTRY MUSING

SOLUTION SET 5

1. **(b)** : We know that, $\Delta T_f = i \times K_f \times m$ ...(i)

Molality may be taken as molarity because it is a solution of monobasic acid.

Substituting the values in equation (i), we get

$0.06 = i \times 1.86 \times 3 \times 10^{-2}$

$\Rightarrow \quad i = \dfrac{0.06}{1.86 \times 3 \times 10^{-2}} = 1.0753$

Let the acid is MH

	MH	$\rightleftharpoons$	M^-	+	H^+
Initial moles	C		0		0
At equilibrium	$C(1-\alpha)$		$C\alpha$		$C\alpha$

$K_a = \dfrac{C\alpha \times C\alpha}{C(1-\alpha)} = C\alpha^2 \qquad (\because\ \alpha << < 1)$

$i = \dfrac{\text{Total moles after dissociation}}{\text{Initial moles}}$

$i = \dfrac{C(1-\alpha) + C\alpha + C\alpha}{C} = 1 + \alpha$

$\alpha = i - 1 = 1.0753 - 1 = 0.0753$

$K_a = C\alpha^2 = 3 \times 10^{-2} \times (0.0753)^2$

$\Rightarrow \quad K_a = 1.70 \times 10^{-4}$

$pK_a = -\log K_a = -\log (1.70 \times 10^{-4})$

$\Rightarrow \quad pK_a = +3.769$

2. **(b)** : Greater the formal charge distribution on each P—H bond lesser is the covalent character.

Formal charge distribution

$= \dfrac{\text{Total charge}}{\text{Number of P–H bonds}}$

In PH_3, $P_2H_6^{2+}$, $P_2H_5^+$, PH_4^+ formal charge distribution on each P—H bond = 0 , 0.33, 0.2, 0.25 respectively.

Thus in $P_2H_6^{2+}$, P–H bond has least covalent character as it has high formal charge distribution.

3. **(a)** : $2KMnO_4 + 16HCl \xrightarrow[\text{conc.}]{} 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2$

$NaCl + H_3PO_4 \longrightarrow NaH_2PO_4 + HCl$

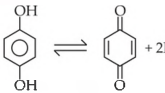
MnO_2 reacts with conc. HCl to produce Cl_2, not with NaCl,

$MnO_2 + 4HCl \xrightarrow[\text{conc.}]{} MnCl_2 + 2H_2O + Cl_2$

As Br_2 is weaker oxidising agent than Cl_2 it cannot displace Cl_2 from CCl_2.

4. **(b)** : Compounds (1), (3), (5) have active methylene group, hence can be extensively enolised.

5. **(c)** :



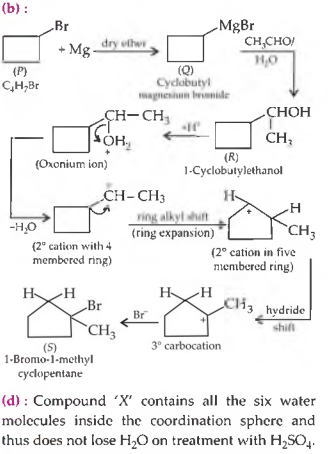
$E = E° - \dfrac{0.0591}{2}\log[H^+]^2$

$= E° - \dfrac{0.0591}{2} \times 2\log[H^+] \qquad [\because -\log [H^+] = pH]$

$= E° + \dfrac{0.0591}{2} \times 2pH = E° + 0.0591\ pH$

$= 1.30 + 0.0591 \times 2 = 1.30 + 0.1182 = 1.42\ V$

6. **(b)** :



7. **(d)** : Compound 'X' contains all the six water molecules inside the coordination sphere and thus does not lose H_2O on treatment with H_2SO_4.

8. **(a)** : Complex 'Z' has two water molecules outside the sphere which on treatment with H_2SO_4 gives

$\dfrac{\text{Weight of } H_2O \text{ molecules lost}}{\text{Molar mass of complex}} \times 100 = \dfrac{36}{266.5} \times 100$

$= 13.5\%$

loss in weight.

9. **(3)** : Relative number of atoms of

$C = \dfrac{60}{12} = 5$; $H = \dfrac{13.3}{1.008} = 13.2$; $O = \dfrac{26.7}{16} = 1.67$

Atomic ratio is C : H : O = $\frac{5}{1.67} : \frac{13.2}{1.67} : \frac{1.67}{1.67}$

$= 3 : 8 : 1$

Hence, empirical formula is C_3H_8O.

$\Rightarrow$ Empirical formula mass = 60

As molecular mass = 2 × Vapour density

$= 2 \times 30 = 60$

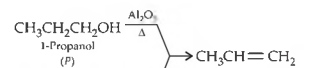
So, the molecular formula is also C_3H_8O.

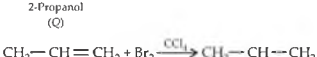
Hence, the two alcohols '*P*' and '*Q*' are

$CH_3CH_2CH_2OH$ and $CH_3-\underset{\underset{OH}{|}}{CH}-CH_3$

Propan-1-ol (*P*) Propan-2-ol (*Q*)

They are dehydrated to propene, when passed over heated alumina. Propene decolourises the reddish brown colour of bromine solution in CCl_4.





Sum of positions = 1 + 2 = 3

10. **(4)** : Let the volumes of CH_4, C_2H_4 and C_2H_2 at N.T.P. = x, y and z mL respectively.

From question, $x + y + z = 10$ ...(i)

As we know that

Weight of CH_4 + Weight of C_2H_4 + Weight of C_2H_2 = Weight of mixture

$$\frac{16x}{22400} + \frac{28y}{22400} + \frac{26z}{22400} = \frac{2 \times 11.3}{22400} \times 10 \quad \text{...(ii)}$$

Now, $\underset{x\text{ mL}}{CH_{4(g)}} + 2O_{2(g)} \rightleftharpoons CO_{2(g)} + 2H_2O_{(l)}$

$\underset{y\text{ mL}}{C_2H_{4(g)}} + \underset{3y\text{ mL}}{3O_{2(g)}} \rightleftharpoons 2CO_{2(g)} + 2H_2O_{(l)}$

$\underset{z\text{ mL}}{C_2H_{2(g)}} + \underset{\frac{5}{2}z\text{ mL}}{\frac{5}{2}O_{2(g)}} \rightleftharpoons 2CO_{2(g)} + H_2O_{(l)}$

Total volume of oxygen used up in the reaction

$$= \left(2x + 3y + \frac{5}{2}z\right) \text{mL}$$

But from question,

Total volume of oxygen used up = 30 – 5.5

= 24.5 mL

$\therefore \quad 2x + 3y + \frac{5}{2}z = 24.5$ ...(iii)

Solving equations (i), (ii) and (iii), we get

$x = 4$, $y = 3$, $z = 3$.

$\therefore$ $CH_4 = 4$ mL, $C_2H_4 = 3$ mL, $C_2H_2 = 3$ mL

❑❑

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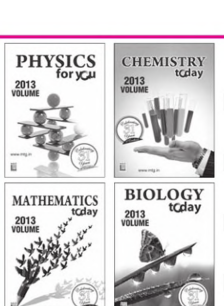

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EXAMINER'S MIND NCERT CLASS XII

The questions given in this column have been prepared strictly on the basis of NCERT Chemistry for Class XII. This year JEE (Main & Advanced)/AIPMT/AIIMS /other PMTs have drawn their papers heavily from NCERT books.

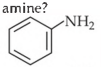
AMINES | BIOMOLECULES | POLYMERS | CHEMISTRY IN EVERYDAY LIFE

SECTION - I

Only One Option Correct Type

This section contains 20 multiple choice questions. Each question has four choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

1. Which of the following is 3° amine?

(a)
(b) 
(c)
(d)

2. Polymerisation of caprolactam yields
(a) terylene (b) nylon-6
(c) nylon-6, 6 (d) polyethene.

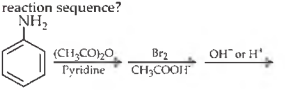
3. Product formed on oxidation of gluconic acid with nitric acid is
(a) *n*-hexane (b) saccharic acid
(c) sucrose (d) cellulose.

4. Which of the following will not undergo Hinsberg's test?
(a) 1° amine (b) 2° amine
(c) 3° amine (d) Both (a) and (b)

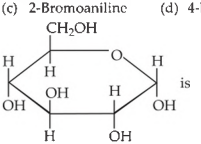
5. Which of the following statements is correct?
(a) Some tranquilisers function by inhibiting the enzymes which catalyse the degradation of noradrenaline.
(b) Tranquilisers are narcotic drugs.
(c) Tranquilisers are chemical compounds that do not affect the message transfer from nerve to receptor.
(d) Tranquilisers are chemical compounds that can relieve pain and fever.

6. Monomers of bakelite are
(a) urea and formaldehyde
(b) phthalic acid and ethylene glycol
(c) phenol and formaldehyde
(d) 1, 3-butadiene and acrylonitrile.

7. What will be the final product of the following reaction sequence?



(a) 2, 4, 6-Tribromoaniline
(b) 2, 4-Dibromoaniline
(c) 2-Bromoaniline (d) 4-Bromoaniline

8.  is

(a) Fischer projection formula of α-*D*-glucose
(b) Fischer projection formula of β-*D*-glucose
(c) Haworth projection formula of α-*D*-glucose
(d) Haworth projection formula of β-*D*-glucose.

9. $C_6H_5NH_2 \xrightarrow[0\text{-}5°C]{NaNO_2 + HCl} (X) \xrightarrow{CuCN} (Y)$

X and Y in the above reaction sequence are respectively
(a) $C_6H_5NHCH_3$, C_6H_5CN
(b) $C_6H_5N_2^+Cl^-$, C_6H_6
(c) $C_6H_5NH_3Cl^-$, C_6H_5OH
(d) $C_6H_5N_2^+Cl^-$, C_6H_5CN

10. Aspartame is one of the good artificial sweeteners whose use is limited to cold foods and soft drinks because
(a) aspartame has very high boiling point
(b) aspartame gets dissociated at cooking temperature

(c) aspartame is sweetener at low temperatures only
(d) aspartame is not soluble at higher temperatures.

11. Natural rubber is considered as a linear polymer of
(a) isoprene (b) chloroprene
(c) neoprene (d) Both (a) and (b).

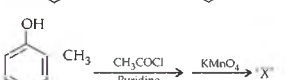
12. Dettol is used as an antiseptic. It is a mixture of
(a) furacine, terpineol
(b) bithionol, iodoform
(c) chloroxylenol, terpineol
(d) veronal, serotonin.

13. In vulcanisation of rubber
(a) sulphur reacts to form a new compound
(b) sulphur cross-links are introduced
(c) sulphur forms a very thin protective layer over rubber
(d) all statements are correct.

14. Which of the following polymer is stored in the liver of animals?
(a) Amylose (b) Cellulose
(c) Amylopectin (d) Glycogen

15. Which of the following compounds is the weakest Bronsted base?

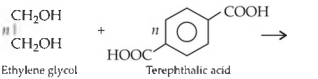
(a)
(b)
(c)
(d)

16. 

The final product '*X*' is a medicine. Which of the following is incorrect regarding '*X*'?
(a) It is analgesic with antipyretic properties.
(b) It helps to prevent heart attack.
(c) It suppresses the gastric anomalies.
(d) It has anti-blood clotting action.

17. Which of the following is not optically active?
(a) Glycine (b) Tyrosine
(c) Lysine (d) Alanine

18. Name of the polymer formed by given condensation reaction is



(a) glyptal (b) buna-N
(c) PHBV (d) dacron

19. Who discovered the antibacterial properties of a *Penicillium* fungus?
(a) Alexander Fleming (b) Paul Ehrlich
(c) Watson—Crick (d) Chargaff

20. Deficiency of which vitamin causes cheilosis?
(a) Vitamin B_6 (b) Vitamin B_{12}
(c) Vitamin B_2 (d) Vitamin B_1

SECTION - II

One or More Options Correct Type

This section contains 5 multiple choice questions. Each question has four choices (a), (b), (c) and (d), out of which ONE or MORE are correct.

21. Which of the following are antidepressants?
(a) Equanil (b) Iproniazid
(c) Phenelzine (d) Chlordiazepoxide

22. A positive carbylamine test is given by
(a) *N*, *N*-dimethylaniline
(b) 2, 4-dimethylaniline
(c) *N*-methyl-*o*-methylaniline
(d) *p*-methylbenzylamine

23. Amino acids are classified as acidic, basic or neutral depending upon the relative number of amino and carboxyl groups in their molecule. Which of the following are basic?
(a) $(CH_3)_2CH-\underset{\displaystyle NH_2}{\underset{|}{CH}}-COOH$
(b) $H_2N-CH_2-CH_2-\underset{\displaystyle NH_2}{\underset{|}{CH}}-COOH$
(c) $H_2N-CH_2-\underset{\displaystyle COOH}{\underset{|}{CH}}-CH_2-NH_2$
(d) $HOOC-CH_2-\underset{\displaystyle NH_2}{\underset{|}{CH}}-COOH$

24. Which of the following is/are addition polymer(s)?
(a) Buna-S (b) Neoprene
(c) Teflon (d) PVC

25. The reagents that can be used to convert benzenediazonium chloride to benzene are
(a) $SnCl_2/HCl$ (b) CH_3CH_2OH
(c) H_3PO_2, H_2O (d) HBF_4

SECTION - III

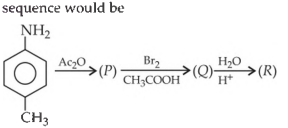
Paragraph Type

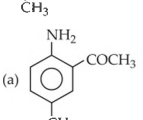
This section contains 2 paragraphs each describing theory, experiment, data, etc. Six questions relate to two paragraphs with three questions on each paragraph. Each question of a paragraph has only one correct answer among the four choices (a), (b), (c) and (d).

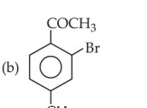
Paragraph for Questions 26 to 28

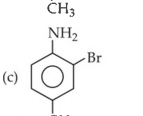
Aliphatic and aromatic primary and secondary amines react with acid chlorides, anhydrides and esters by nucleophilic substitution reaction. This reaction is known as acylation. This reaction is the replacement of hydrogen atom of $-NH_2$ or $>N-H$ group by the acyl group. The products obtained by acylation reaction are known as amides. The reaction is carried out in the presence of a base stronger than the amine, like pyridine, which removes HCl so formed and shifts the equilibrium to the right hand side.

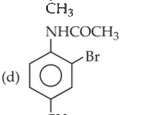
26. The product (*R*) in the following reaction sequence would be



(a) 

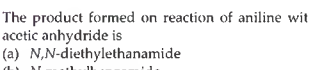
(b) 

(c) 

(d) 

27. The product formed on reaction of aniline with acetic anhydride is

(a) *N*,*N*-diethylethanamide
(b) *N*-methylbenzamide
(c) acetanilide (d) None of these.

28. 

P, *Q* and *R* in the given reaction are respectively

(a) benzonitrile, benzamide, *m*-nitrobenzene
(b) acetanilide, *m*-nitroacetanilide, *m*-nitroaniline
(c) benzonitrile, *p*-nitrobenzamide, *p*-nitrobenzene
(d) acetanilide, *p*-nitroacetanilide, *p*-nitroaniline

Paragraph for Questions 29 to 31

The repeating structural units are derived from some simple and reactive molecules known as monomers and are linked to each other by covalent bonds. This process of formation of polymers from respective monomers is called polymerisation. The addition polymers are formed by the repeated addition of monomer molecules possessing double or triple bonds. The condensation polymers are formed by repeated condensation reaction between two different bi-functional or tri-functional monomeric units. In these polymerisation reactions, the elimination of small molecules such as water, alcohol, hydrogen chloride, etc. takes place.

29. Which of the following is not formed by condensation polymerisation?

(a) Melamine-formaldehyde polymer
(b) Novolac
(c) Buna-N
(d) PHBV

30. Which set of the compounds is used in the manufacture of nylon-6, 6?

(a) $HOOC(CH_2)_4COOH + H_2N(CH_2)_6NH_2$
(b) $CH_2=CH-C(CH_3)=CH_2$
(c) $H_2C=CH_2 + H_2C=CH-CN$
(d) $HOOC(CH_2)_8COOH + H_2N(CH_2)_6NH_2$

31. Acrilan is a hard, horny and high melting material. Which of the following represents its structure?

(a)

(b)

(c)

(d)

SECTION - IV
Matching List Type

This section contains 3 multiple choice questions. Each question has matching lists. The codes for the lists have choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

32. Match the List I with the List II and select the correct answer using the code given below the lists:

List I	List II
P. Isoleucine	1. Carbohydrate
Q. Cellulose	2. Protein
R. Myosin	3. Vitamin
S. Ascorbic acid	4. Amino acid

	P	Q	R	S
(a)	4	3	2	1
(b)	1	2	3	4
(c)	4	1	2	3
(d)	3	2	1	4

33. Match the polymers given in List I with the type of linkage present in them given in List II and select the correct answer using the code given below the lists:

List I	List II
P. Terylene	1. Glycosidic linkage
Q. Nylon-6, 6	2. Ester linkage
R. Cellulose	3. Phosphodiester linkage
S. RNA	4. Amide linkage

	P	Q	R	S
(a)	2	4	1	3
(b)	1	2	3	4
(c)	3	1	2	4
(d)	4	2	1	3

34. Match the List I with the List II and select the correct answer using the code given below the lists:

List I	List II
P. Seldane	1. Artificial sweetener
Q. Novestrol	2. Tranquiliser
R. Meprobamate	3. Antihistamine
S. Alitame	4. Antifertility drug

	P	Q	R	S
(a)	3	1	2	4
(b)	4	2	1	3
(c)	1	2	3	4
(d)	3	4	2	1

SECTION - V
Assertion-Reason Type

In the following questions, a statement of assertion is followed by a statement of reason. Mark the correct choice as :

(a) If both assertion and reason are true and reason is the correct explanation of assertion.
(b) If both assertion and reason are true but reason is not the correct explanation of assertion.
(c) If assertion is true but reason is false.
(d) If both assertion and reason are false.

35. **Assertion :** *N, N*-Diethylbenzenesulphonamide is insoluble in alkali.
Reason : Sulphonyl group attached to nitrogen atom is strong electron withdrawing group.

36. **Assertion :** Competitive inhibitors compete with natural substrate for their attachment on the active sites of enzymes.
Reason : In competitive inhibition, inhibitor binds to the allosteric site of the enzyme.

37. **Assertion :** Polyamides are best used as fibres because of high tensile strength.
Reason : Strong intermolecular forces (like hydrogen bonding within polyamides) lead to close packing of chains and increase the crystalline character, hence, provide high tensile strength to polymers.

38. **Assertion :** The hydrolysis of sucrose shows optical inversion.
Reason : The hydrolysis of sucrose involves conversion of α-glycosidic linkage to β-glycosidic linkage.

39. **Assertion :** Artificial sweeteners are added to the food to control the intake of calories.
Reason : Most of the artificial sweeteners are inert and do not metabolise in the body.

40. **Assertion :** Benzenediazonium ion couples with aniline effectively in a weakly acidic medium.
Reason : In a weakly acidic medium, the aniline becomes respectively more activated for electrophilic substitution.

SECTION - VI
Integer Value Correct Type

This section contains 10 questions. The answer to each question is a single digit integer, ranging from 0 to 9 (both inclusive).

41. The number of amines that are possible for the compound with formula C_3H_9N is

42. Among the following polymers, total number of condensation copolymers is
Nylon-6,6, Buna-S, PVC, Dacron, Bakelite, Natural rubber, Buna-N, PHBV, Glyptal

43. Out of the following, total number of amines those will undergo diazotisation is
N,N-Dimethylethanamine, Aniline, *p*-Bromoaniline, 2, 4, 6-Tribromoaniline, *tert*-Butylamine

44. A heptapeptide contains x peptide linkages. The value of x is

45. Out of the following, total number of thermosetting polymers is
Polythene, Bakelite, PVC, Melamine-formaldehyde resin, Polystyrene, Urea-formaldehyde resin, Nylon-6,6, Dacron

46. The number of tetrapeptides formed by four different amino acids is

47. Out of the following, the total number of antihistamine drugs is
Dimetapp, Phenelzine, Alitame, Equanil, Novestrol, Morphine, Seldane, Bithionol.

48. The total number of acidic groups in aspartic acid is

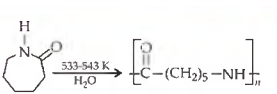
49. In chemistry, same substances can act as an antiseptic as well as disinfectant by varying the concentration. 0.2% solution of phenol is an antiseptic while its y% solution is disinfectant. The value of y is

50. Cetyltrimethylammonium bromide is a popular cationic detergent and is used in hair conditioners. It is z° amine. The value of z is

SOLUTIONS

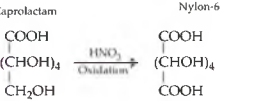
1. **(a)**

2. **(b) :**



Caprolactam — Nylon-6

3. **(b) :**



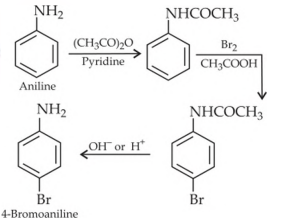
Gluconic acid — Saccharic acid

4. **(c) :** 3° amines do not react with benzenesulphonyl chloride (Hinsberg's reagent) due to absence of hydrogen atoms attached to nitrogen atom.

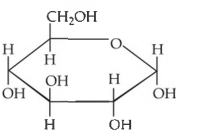
5. **(a)**

6. **(c)**

7. **(d) :**



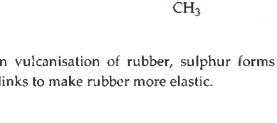
8. **(c) :** The cyclic structure of α-*D*-glucose represents Haworth projection formula.



9. **(d) :** $C_6H_5NH_2 \xrightarrow[0\text{-}5°C]{NaNO_2 + HCl} \underset{(X)}{C_6H_5N_2^+Cl^-} \xrightarrow{CuCN} \underset{(Y)}{N_2 + C_6H_5CN}$

10. **(b) :** Aspartame is unstable at cooking temperature thus gets dissociated.

11. **(a) :** Natural rubber is a linear polymer of isoprene (2-methyl-1, 3-butadiene) and it is also known as *cis*-1, 4-polyisoprene.



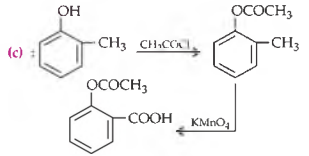
12. **(c)**

13. **(b) :** In vulcanisation of rubber, sulphur forms cross-links to make rubber more elastic.

14. **(d)**

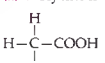
15. **(c) :** Amines are stronger bases than phenols and alcohols. Since phenol is more acidic than alcohol, thus, phenol has the least tendency to accept a proton and hence it is weakest Bronsted base.

16. **(c)** :

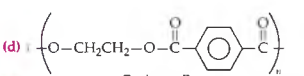


(X)
o-Acetylsalicylic acid
(Aspirin)

17. **(a)** : Glycine is optically inactive.



18. **(d)** :



Terylene or Dacron

19. **(a)**

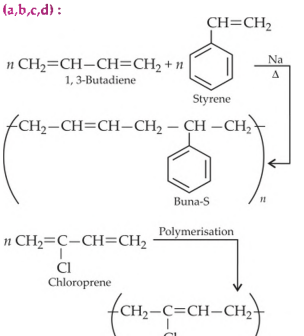
20. **(c)** : Deficiency of vitamin B_2 (Riboflavin) causes cheilosis (fissuring at corners of mouth and lips).

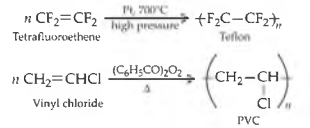
21. **(a,b,c,d)**

22. **(b,d)** : The carbylamine reaction is given by only primary amines. Hence 2, 4-dimethylaniline and *p*-methylbenzyl amine will give this test.

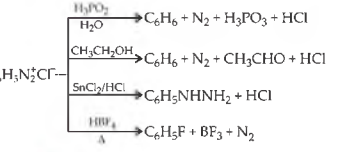
23. **(b,c)** : In (b) and (c) number of amino($-NH_2$) groups is more than number of carboxyl ($-COOH$) groups hence, are basic.

24. **(a,b,c,d)** :

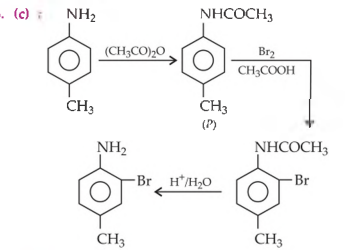




25. **(b,c)** :



26. **(c)** :



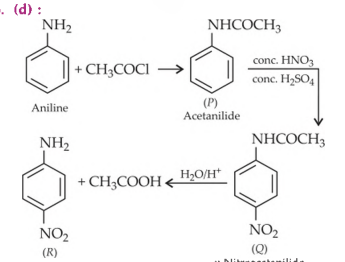
27. **(c)** : $C_6H_5NH_2 + (CH_3CO)_2O$

Aniline Acetic anhydride

$C_6H_5NHCOCH_3 + CH_3COOH$

N-Phenylethanamide
(Acetanilide)

28. **(d)** :



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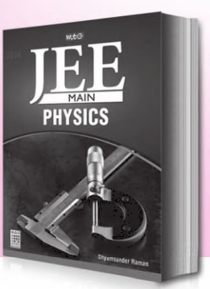

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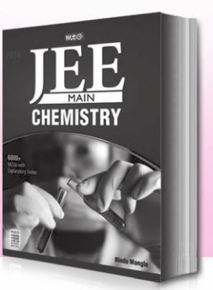

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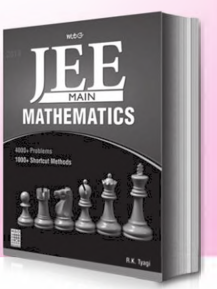

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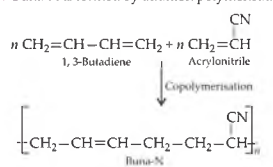
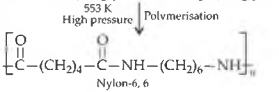
29. **(c)** : Buna-N is formed by addition polymerisation.



30. **(a)** : $n\ HOOC(CH_2)_4COOH + n\ H_2N(CH_2)_6NH_2$



31. **(a)** : Acrilan or orlon is a polymer of acrylonitrile.

32. **(c)** : (P) Isoleucine is an amino acid.
(Q) Cellulose is a carbohydrate. It is a predominant constituent of cell wall of plant cells.
(R) Myosin is a fibrous protein present in muscles.
(S) Vitamin C is an ascorbic acid.

33. **(a)** 34. **(d)**

35. **(b)** : Since *N,N*-diethylbenzene sulphonamide does not contain any hydrogen atom attached to nitrogen atom, it is not acidic and hence insoluble in alkali.

36. **(c)** : In competitive inhibition, inhibitor binds to the active site of the enzyme.

37. **(a)**

38. **(c)** : Hydrolysis of sucrose involves conversion of sucrose (dextrorotatory) into the mixture of glucose (dextro) and fructose (laevo).

39. **(a)**

40. **(c)** : The activity of aniline, though decreases but the activity of diazonium ion increases.

41. **(4)** : $CH_3CH_2CH_2NH_2$, Propan-1-amine (1°)

$CH_3-\underset{\underset{NH_2}{|}}{CH}-CH_3$, Propan-2-amine (1°)

$CH_3CH_2NHCH_3$, *N*-Methylethanamine (2°)

$CH_3-\underset{\underset{CH_3}{|}}{N}-CH_3$, *N, N*-Dimethylmethanamine (3°)

42. **(5)** : Buna-S, PVC, natural rubber, Buna-N are the examples of addition polymerisation.

43. **(3)** : Aromatic diazonium salts are much more stable than aliphatic diazonium salts.

44. **(6)** : The peptide bond is formed between two amino acids by the elimination of a water molecule. A dipeptide contains one peptide linkage. A tripeptide contains two peptide linkages. Similarly, a heptapeptide contains six peptide linkages.

45. **(3)** : Bakelite, urea-formaldehyde resin and melamine-formaldehyde resin are thermosetting polymers.
Nylon-6,6 and dacron are fibres. Polythene, PVC and polystyrene are thermoplastic polymers.

46. **(8)** : Since each amino acid has one N-terminal end and one C-terminal end, therefore, four different amino acids will form $2 \times 4 = 8$ different tetrapeptides.

47. **(2)** : Phenelzine and equanil are tranquilisers and morphine is narcotic analgesic and bithionol is an antiseptic. Alitame is used as an artificial sweetening agent. Novestrol is an antifertility drug. Dimetapp and seldane are antihistamines.

48. **(2)** : $HOOC-CH_2-\underset{\underset{NH_2}{|}}{CH}-COOH$
Aspartic acid

49. **(1)** : 1% solution of phenol is disinfectant.

50. **(4)** : It is a quarternary salt.

$$\left[CH_3(CH_2)_{15}-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{N}}-CH_3\right]^{+}Br^{-}$$

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MONTHS	Solved Papers (2013)	Practice Papers (2013 & 2014)	Examiner's Mind	JEE Foundation Series	Concept Map	Others
JANUARY		JEE Main, JEE Advanced, CBSE Board Chapterwise Series-8 (2013)	Hydrocarbons, Environmental Chemistry (Class XI); Amines, Biomolecules, Polymers, Chemistry in Everyday Life (Class XII)	Unit-7 : Organic Compounds Containing Oxygen, Organic Compounds Containing Nitrogen	Surface Chemistry	NCERT Xtract, NEET Special (Scrapbook), Interview FIITJEE
FEBRUARY		JEE Main, Practice Problems JEE Advanced, NEET, CBSE Board Chapterwise Series-9 (2013)		Unit-8 : Polymers, Biomolecules, Chemistry in Everyday Life	Organic Compounds Containing oxygen-I	NCERT Xtract, NEET Special (Scrapbook), Co, discuss & Discover
MARCH		JEE Main, JEE Advanced, NEET, CBSE Board Sample Paper (2013)		Unit-9 : Practical Chemistry	Organic Compounds Containing oxygen-II	NCERT Xtract, Brain Booster (Inorganic Chemistry), NEET Special (Scrapbook), Quick Revision of Physical Chemistry
APRIL	CBSE Board	JEE Advanced, Odisha JEE NEET, AIIMS (2013)			Organic Compounds Containing Nitrogen	NCERT Xtract, Brain Booster (Physical Chemistry), Concept Booster, NEET Special (Scrapbook), AIIMS Special (Assertion & Reason), Quick Revision of Inorganic Chemistry (Part-I)
MAY	JEE Main	JEE Advanced, AIIMS, Target PMTs (2013)			Biomolecules	NCERT Xtract, Concept Booster, NEET Special (Scrapbook), AIIMS Special (Assertion & Reason), Quick Revision of Inorganic Chemistry (Part-II), Brainstorming Problems (Physical Chemistry)
JUNE	Kerala PET, WB JEE (Engg.), NEET	CBSE Board Chapterwise Series-1 (2014)			General Principles and Processes of Isolation of Elements	NCERT Xtract, Competition Corner (Physical Chemistry), Curiosity Corner, Why & How? (Inorganic Chemistry), Learn Fast (Hydrogen and its Compounds), Resonance and its Effects, Chemistry Olympiad Problems, High yield Facts (Some Basic Concepts of Chemistry and Structure of atom)
JULY	JEE Advanced, Karnataka CET, AMU (Medical)	CBSE Board Chapterwise Series-2 (2014)	Some Basic Concepts of Chemistry, Structure of Atom (Class XI); The Solid State, Solutions (Class XII)	Unit-1 :Some Basic Concepts in Chemistry, States of Matter, Atomic Structure, Chemical Bonding and Molecular Structure	Hydrogen and its Compounds	Concept Booster, Competition Corner (Physical Chemistry) : Atomic Structure (Class XI); Solutions (Class XII)
AUGUST		CBSE Board Chapterwise Series-3 (2014)	Classification of Elements and Periodicity in Properties, Chemical Bonding and Molecular Structure (Class XI); Electrochemistry, Chemical Kinetics (Class XII)	Unit-2 : Chemical Thermodynamics, Solutions, Equilibrium	s-Block Elements	NCERT Xtract, Concept Booster, Competition Corner (Physical Chemistry) : Atomic Structure and solutions - Continued, Learn Fast (Some Basic Principles of Organic Chemistry), Chemistry Musing Problem Set-1
SEPTEMBER	J & K CET	CBSE Board Chapterwise Series-4 (2014)	States of Matter, Thermodynamics (Class XI), Surface Chemistry, General Principles and Processes of Isolation of Elements (Class XII)	Unit-3 : Redox Reactions, Electrochemistry, Chemical Kinetics, Surface Chemistry	p-Block Elements (Group 13, 14 and 15)	NCERT Xtract, Concept Booster, Competition Corner : Gaseous state (Class XI); Coordination Complexes (Class XII), Learn Fast (Alcohols, Phenols & Ethers), Chemistry Musing Problem Set-2, Chemistry Musing Solution Set-1
OCTOBER	AMU (Engg.)	CBSE Board Chapterwise Series-5 (2014)	Equilibrium, Redox Reactions (Class XI); The p-Block Elements (Group 15 to 18), the d- and f-Block Elements (Class XII)	Unit-4 : Classification of Elements and Periodicity in Properties, Metallurgy, Hydrogen, s-Block Elements, p-Block Elements (Groups 13 and 14)	p-Block Elements (Group 16, 17 and 18)	NCERT Xtract, Concept Booster, Essential Formulae for Competitive Exams, Learn Fast (Aldehydes, Ketones and Carboxylic acids), You asked, we Answered, Chemistry Musing Problem Set-3, Chemistry Musing Solution Set-2
NOVEMBER		CBSE Board Chapterwise Series-6 (2014)	Hydrogen, The s-Block Elements, (Class XI) ; Coordination Compounds, Haloalkanes and Haloarenes (Class XII)	Unit-5 : p-Block Elements (Group 15 to 18), d- and f-Block Elements, Coordination Compounds, Environmental Chemistry	d- and f- Block Elements	NCERT Xtract, Concept Booster, Competition Corner (Organic Chemistry), Learn Fast (States of Matter), You asked, we Answered: Chemistry Musing Problem Set-4, Chemistry Musing Solution Set-3
DECEMBER		CBSE Board Chapterwise Series-7 (2014)	The p-Block Elements, Organic Chemistry - Some Basic Principles and Techniques (Class XI); Alcohols, Phenols and Ethers, Aldehydes, Ketones and Carboxylic Acids (Class XII)	Unit-6 : Purification and Characterisation of Organic Compounds, Some Basic Principles of Organic Chemistry, Hydrocarbons, Organic Compounds Containing Halogens	Redox Reactions & Electrochemistry	NCERT Xtract, Concept Booster, Competition Corner (Organic Chemistry), You asked, we Answered, Chemicals in Action, Chemistry Musing Problem Set-5, Chemistry Musing Solution Set-4

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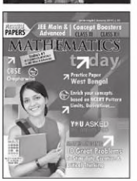

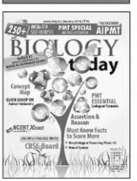

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